APPLICATION OF GREEN'S FUNCTION TECHNIQUE TO PARAMAGNETIC RESONANCE

by

BARRY FRANK

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M.Sc., McGill University, 1962

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ABSTRACT

This thesis contains discussions of a number of points which arose when the author was studying the "paramagnetic resonance line shape problem". The so-called moment method is discussed, and a new derivation of the moments of the line shape function is given. Single-spin operators are introduced which simplify the calculation of these moments. The Green's function technique, as applied to this problem, and the decoupling approximations associated with the technique, are looked at from the point of view of reliability and complexity. As a test of the reliability of any decoupling, a theorem concerning the moments of a line shape arising from such a decoupling is discussed and proved. The Green's function technique is applied to the case of the one-dimensional Ising model with spin ½, where no decoupling of the hierarchy of Green's function equations is necessary. A method of calculating thermal averages for this case, using difference equations, is given.

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CHAPTER I

Introduction and Summary

This thesis contains discussions of a number of points which arose when the author was studying the "paramagnetic resonance line shape problem." This problem is one which has long defied attempts at solution and we do not succeed in solving it. However, some points arose which it was thought were, in themselves, worthy of discussion. The motivation for tackling the problem was that with the recently introduced techniques of double-time temperature-dependent Green's functions, some hope of solution might be entertained.

Let us first briefly review the problem (details are given in Chapter II). The physical system consists of a crystalline sample containing N identical paramagnetic unit systems or "spins". This system is acted on by a constant magnetic field $\underline{H}_0$. As a result the system has a certain number of eigenstates, and transitions between these eigenstates can be induced by a high-frequency oscillating magnetic field $\underline{H}_1(t) = \underline{H}_1 \cos \omega t$. The resulting absorption of the high-frequency radiation is referred to as paramagnetic resonance absorption and the problem is to calculate, from first principles, the shape of one of the absorption lines. In particular one wishes to know how this shape changes with temperature.

The problem that has been studied is that in which the temperature-dependence of the line shape arises solely from the average occupation numbers of the various energy levels of the system. In the absence of interaction between the unit spin systems, these energy levels would be, except for the lowest and the highest energy levels, highly degenerate. The spin-spin interactions then remove these degeneracies to a certain degree. There exists, therefore, no natural relaxation mechanism that would yield a continuous line shape: the line shape function consists of a series of delta-

functions. One has basically to carry out a quantum-mechanical calculation to find the energy levels, and then to follow this with a statistical-mechanical treatment to find occupation probabilities. With the inclusion of other thermal effects (e.g. lattice vibrations), one would be led to broadened temperature-dependent energy levels and perhaps a continuous line shape. We do not discuss this aspect of the problem.

The Hamiltonian of the system consists of three terms: (a) a spin Hamiltonian which is the sum of the Hamiltonians of the individual paramagnetic units in the presence of the applied constant magnetic field and the crystalline field; (b) a spin-spin interaction which consists of a dipole-dipole interaction and an exchange interaction; (c) the interaction with the applied oscillating magnetic field. With no crystalline field present, the energy levels of the individual spins are equally spaced, with spacing $\hbar\omega_0$ say. The absorption spectrum then consists of a set of lines at frequencies $0, W_0, 2W_0, 3W_0, \ldots$ and to single out the primary line at W_0 one does a truncation of the spin-spin interaction (Van Vleck, 1948). If a crystalline field is present and the effective spin is greater than one-half, then in general the individual spin levels for part (a) of the Hamiltonian will not be equally spaced. One then obtains a set of primary lines (with their associated secondary ones). A truncation of part (c) of the Hamiltonian is then required (Kambe and Usui, 1952) to single out a particular primary line. This latter truncation has been performed (Pryce and Stevens, 1950); McMillan and Opechowski, 1960) using projection operators which pick out eigenstates of the full Hamiltonian of part (a). It is possible to carry out the second truncation (Kambe and Usui) using operators defined in the representation of single-spin eigenfunctions. These latter operators are introduced in Chapter II of this thesis.

The authors mentioned above (Van Vleck, Kambé and Usui, McMillan and Opechowski) did not attempt to calculate the line shape but contented themselves with calculating its low moments (first and second). This is referred to as the moment method, and little can be said from these moments concerning the line shape itself. We show in Chapter IV that our single-spin operators simplify the calculation of these moments.

In recent years, the technique of double-time temperature-dependent Green's functions has been used to calculate line shapes directly, and the motivation of this work was to find if this technique was of value in the paramagnetic resonance line shape problem. As a preliminary exercise, the line shape function for the one-dimensional Ising model with spin ½ and nearest-neighbour interactions was studied and is discussed in Chapter III. In this case no decoupling of the hierarchy of Green's function equations is necessary.

The technique has been applied by Tomita and Tanaka (1963) to the case in which no crystalline field is present. Their decoupling procedure is designed to make the resulting closed set of equations as tractable as possible. Our attempt at decoupling is designed to be as reliable as possible, but unfortunately gives rise to a set of equations which we have not been able to solve. As a test of the reliability of any decoupling, a theorem concerning the moments of a line shape arising from such a decoupling was used, and is discussed and proved in Chapter V. Decoupling approximations are also discussed in Chapter V. The result of our decoupling is given in Chapter VI and compared with that of Tomita and Tanaka (1963).

These decouplings of course lead to a set of delta-functions for the line shape, and Tomita and Tanaka derived a continuous line shape by introducing rather arbitrarily a smearing of delta-functions. This aspect

of the problem is also discussed in Chapter VI where the general Ising model is used as an illustrative example.

For a treatment of the problem in which the individual spin energy levels are not equidistant, the individual spin operators previously mentioned were used; it was for this problem that they were originally introduced. This problem proved intractable and the reasons for this are discussed, also in Chapter VI.

CHAPTER II

General Formalism

1. System Hamiltonian

Our physical system consists of a crystalline sample containing N identical paramagnetic electronic unit systems, or "spins", possessing magnetic moments. It is assumed that the sample has been placed in a constant magnetic field $\underline{H}_0$ and a high frequency oscillating magnetic field $\underline{H}_1(t) = \underline{H}_1 \cos(\ t)$ perpendicular to $\underline{H}_0$. Each spin is defined by a "spin-Hamiltonian" $H_i^{(o)}$ which incorporates the effect of the external constant magnetic field and of any arbitrary crystalline electric field that may be present. The oscillating magnetic field induces transitions between the energy states of the spin system, and experimentally, we find that energy is absorbed from the oscillating field. The "line shape problem" consists of finding the power absorbed by the spin system as an analytic function of ω, the frequency of the oscillating field.

In addition to the interaction of the spins with the two magnetic fields and with the crystalline electrostatic field, there are weak interactions within the spin system. Were these latter interactions absent, the line-shape would consist only of widely separated delta-function peaks; these "spin-spin interactions" serve to "broaden" the lines, giving them their shape (i.e., closely spaced delta-functions of differing strengths occur, and they are not experimentally resolvable).

Mention must also be made of interactions between the spin system and the lattice. We take it that the temperature is low enough so that the effects of lattice vibrations can always be neglected.

The Hamiltonian describing our paramagnetic system may be written

$$\mathcal{H}_T = \mathcal{H} + \mathcal{H}^{(2)} \tag{2-1}$$

where

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} \tag{2-2}$$

$$\mathcal{H}^{(0)} \gg \mathcal{H}^{(1)} \tag{2-3}$$

$$\mathcal{H}^{(1)} \gg \mathcal{H}^{(2)} \tag{2-4}$$

$\mathcal{H}^{(0)} = \sum_i \mathcal{H}_i^{(0)}$ is the Zeeman, or unperturbed Hamiltonian with i labelling the lattice sites (2-5)

$\mathcal{H}^{(1)} = \frac{1}{2}\sum_{i}\sum_{j\neq i} \mathcal{H}_{ij}^{(1)}$ is the spin-spin interaction Hamiltonian including dipole-dipole and isotropic exchange interactions (2-6)

$\mathcal{H}^{(2)} = -\underline{M}\cdot\underline{H}_1 \cos\omega t$ is the external perturbation, with $\underline{M}$ the magnetic moment of the spin system.

(2-3) and (2-4) are weak-interaction assumptions.

We assume that $\mathcal{H}_i^{(0)}$ possesses axial symmetry, the axis being the direction of $\underline{H}_0$, which we choose to be the z-axis; and that the eigenstates of $\mathcal{H}_i^{(0)}$ are also eigenstates of the operator corresponding to the z-component of the spin.

Before discussing the line-shape function $\sigma(\omega)$ or its moments, we must modify the Hamiltonian in two ways. The term $\mathcal{H}^{(1)}$ in the Hamiltonian must be "truncated" in order to eliminate the weak "secondary" lines from The argument for this has been given by Van Vleck (1948). This truncation consists in keeping only that part of $\mathcal{H}^{(1)}$ (we will call it $\overline{\mathcal{H}^{(1)}}$) which commutes with $\mathcal{H}^{(0)}$; i.e.

$$\left[\overline{\mathcal{H}^{(1)}}, \mathcal{H}^{(0)}\right] = 0 \tag{2-8}$$

We further define

$$\bar{\mathcal{H}} = \mathcal{H}^{(0)} + \bar{\mathcal{H}}^{(1)} = \mathcal{H}^{(0)} + \frac{1}{2} \sum_i \neq \sum_j \bar{\mathcal{H}}_{ij}^{(1)} \tag{2-9}$$

Then

$$[\bar{\mathcal{H}}, \mathcal{H}^{(0)}] = 0 \tag{2-10}$$

Also, when a crystalline electric field is present, and, thus, the energy levels of an unperturbed spin are not in general equidistant, $\mathcal{H}^{(2)}$ must be modified in such a way as to cause transitions between only two levels of a spin. This must be done in order to ensure that other "primary" lines of comparable intensity to the one under consideration, are not included in the calculations. The necessity for this further truncation was pointed out by Kambe and Usui (1952). We let $\hat{\mathcal{H}}^{(2)}$ represent the modified $\mathcal{H}^{(2)}$, and we put a circumflex over its associated operators.

When no crystalline field is present, and $\underline{H}_0$ is in the (-Z)-direction, the Hamiltonian $\bar{\mathcal{H}}_{no\ c.f.}$ is given by equations (2-9), (2-5), and (2-6) with

$$\mathcal{H}_j^{(0)} = -\omega_0 S_j^z \tag{2-11}$$

$$\left(\bar{\mathcal{H}}_{ij}^{(1)}\right)_{no\ c.f.} = A_{ij}\, \underline{S}_i \cdot \underline{S}_j + B_{ij}\, S_i^z S_j^z \tag{2-12}$$

or

$$\left(\bar{\mathcal{H}}_{ij}^{(1)}\right)_{no\ c.f.} = \frac{1}{2} A_{ij} \left(S_i^- S_j^+ + S_j^- S_i^+\right) + C_{ij}\, S_i^z S_j^z \tag{2-12b}$$

where

$$\begin{aligned} C_{ij} &= A_{ij} + B_{ij}\ , \\ A_{ij} = A_{ji} &= \tilde{A}_{ij} + \frac{1}{2} g_\perp^2 \beta^2 r_{ij}^{-3} \left(3\gamma_{ij}^2 - 1\right), \\ B_{ij} = B_{ji} &= -\frac{1}{2} \left(2g_\parallel^2 + g_\perp^2\right) \beta^2 r_{ij}^{-3} \left(3\gamma_{ij}^2 - 1\right); \end{aligned} \tag{2-13}$$

γ_{ij} is the direction cosine of the line of length r_{ij} joining spin i to

spin j relative to the z-axis; $\tilde{A}_{ij}$ are the exchange interaction constants; $g_\perp$ and $g_\parallel$ are the g-factors perpendicular and parallel to the symmetry axis; β is the Bohr magneton;

and

$$\omega_0 = g_\parallel \beta |H_0| > 0 \tag{2-14}$$

is the unperturbed absorption frequency.

Where a crystalline electric field is present, the unperturbed spins have, in general, non-equidistant energy levels. We consider here only those special single-spin Hamiltonians $\mathcal{H}_i^{(0)}$ which have the property that, if $|\lambda\rangle_i$ are the simultaneous eigenstates of S_i^z and $\mathcal{H}_i^{(0)}$ with eigenvalues λ and $-T_\lambda$ respectively, i.e.

$$S_i^z |\lambda\rangle_i = \lambda |\lambda\rangle_i \tag{2-15}$$

$$\mathcal{H}_i^{(0)} |\lambda\rangle_i = -T_\lambda |\lambda\rangle_i \tag{2-16}$$

then

$$T_{\lambda+1} - T_\lambda > 0 \qquad \text{all } \lambda \tag{2-17}$$

Equation (2-17) signifies that in the extension from the no-crystalline field case to the crystalline field case, the order of the unperturbed energy levels, which in both cases are labelled by the eigenvalues of S_i^z, remains unchanged. The statement about non-equidistant energy levels than means that it is not generally true that

$$T_{\lambda'+1} - T_{\lambda'} = T_{\lambda+1} - T_\lambda \tag{2-18}$$

when $\lambda' \neq \lambda$.

The $\overline{\mathcal{H}}_{ij}^{(0)}$ given by equation (2-12) does not any longer commute with $\mathcal{H}^{(0)} = \sum_i \mathcal{H}_i^{(0)}$ where $\mathcal{H}_i^{(0)}$ is defined by (2-16). It must be truncated

still further. The truncation can easily be done if one defines operators $\Delta_{i\lambda}^{\pm}$ by the relation

$$\langle \lambda' | \Delta_{i\lambda}^{\pm} | \lambda'' \rangle_j = \delta_{\lambda\lambda''} \delta_{ij} \langle \lambda' | S_j^{\pm} | \lambda \rangle_j \qquad (2\text{-}19)^{\#}$$

From definition (2-19), equation (2-16), and the well-known commutation relations satisfied by the ordinary ladder operators $S_j^{\pm}$, the following equalities can be derived and are found to be useful:

$$[\Delta_{i\lambda}^{\pm}, S_j^{z}] = \mp \delta_{ij} \Delta_{i\lambda}^{\pm} \qquad (2\text{-}20)$$

$$[\Delta_{i\lambda}^{\pm}, \mathcal{H}^{(0)}] = \left(\overline{I}_{\lambda\pm1} - \overline{I}_{\lambda}\right) \Delta_{i\lambda}^{\pm} \qquad (2\text{-}21)$$

$$\Delta_{i\lambda}^{-} \Delta_{i\lambda'}^{-} = \delta_{\lambda',\lambda+1} \Delta_{i\lambda}^{-} \Delta_{i\lambda+1}^{-} \qquad (2\text{-}22a)$$

$$\Delta_{i\lambda}^{+} \Delta_{i\lambda'}^{+} = \delta_{\lambda',\lambda-1} \Delta_{i\lambda}^{+} \Delta_{i\lambda-1}^{+} \qquad (2\text{-}22b)$$

$$\Delta_{i\lambda}^{+} \Delta_{i\lambda'}^{-} = \delta_{\lambda',\lambda+1} \Delta_{i\lambda}^{+} \Delta_{i\lambda+1}^{-} \qquad (2\text{-}22c)$$

$$\Delta_{i\lambda}^{-} \Delta_{i\lambda'}^{+} = \delta_{\lambda',\lambda-1} \Delta_{i\lambda}^{-} \Delta_{i\lambda-1}^{+} \qquad (2\text{-}22d)$$

With the use of equations (2-20) to (2-22), we find for the crystalline field case

$$\left(\overline{\mathcal{H}}_{ij}^{(1)}\right)_{c.f.} = \frac{1}{2} A_{ij} \sum_{(\lambda',\lambda'') \in G} \left(\Delta_{i\lambda''+1}^{-} \Delta_{j\lambda'}^{+} + \Delta_{j\lambda''+1}^{-} \Delta_{i\lambda'}^{+} \right) + C_{ij} S_i^{z} S_j^{z} \qquad (2\text{-}23)$$

where $\sum_{(\lambda',\lambda'') \in G}$ means summation over all ordered pairs (λ'', λ')

I am indebted to Dr. K. Nishikawa for the suggested use of these operators.

satisfying

$$\overline{T}_{\lambda'+1} - \overline{T}_{\lambda'} = \overline{T}_{\lambda''+1} - \overline{T}_{\lambda''} \qquad (2\text{-}24)$$

Using

$$(\Delta_{i\lambda}^{\pm})^* = \Delta_{i\lambda+1}^{\mp} \qquad (2\text{-}25)$$

which follows from definition (2-19), one can verify that $(\overline{\mathcal{H}}_{ij}^{(i)})_{c.f.}$ is Hermitian. (The asterisk will always be used to denote the Hermitian conjugate).

A Hamiltonian which we consider at some length in a later chapter is that of the Ising model. This Hamiltonian was first proposed by Ising (1925) to describe certain ferromagnetic systems. It turned out not to be valid from a physical point of view, in that it does not describe, with any accuracy, the interactions taking place within any known spin system. However, it is invaluable from a mathematical point of view, in that it is a specialization, of equation (2-12), which is easy to handle.

The model Hamiltonian is given by (2-1), (2-2), (2-5) and (2-6) with

$$\mathcal{H}_j^{(0)} = -\omega_0 S_j^z \qquad (2\text{-}26)$$

$$(\overline{\mathcal{H}}_{ij}^{(i)})_{I.M.} = -\epsilon_{ij} S_i^z S_j^z \qquad (2\text{-}27)$$

where the ϵ_{ij} are the exchange interaction constants. It is seen that (2-27) is just the general paramagnetic resonance Hamiltonian (2-23) with the A_{ij} and the C_{ij} formally put equal to zero and $-\epsilon_{ij}$ respectively.

In many instances a further specialization is useful, namely that of putting

$$\epsilon_{ij} = \begin{cases} \epsilon & i,j \text{ nearest neighbours} \\ 0 & \text{otherwise} \end{cases} \qquad (2\text{-}28)$$

The Hamiltonian with this restriction on the ϵ_{ij} will be called simply the "Ising model Hamiltonian". When this restriction is removed, we will specifically refer to the "general" Ising model Hamiltonian.

These are the only Hamiltonians that will be considered in this thesis. It remains now to exhibit $\hat{\mathcal{H}}_2$ for these various cases.

We have, from equation (2-7),

$$\hat{\mathcal{H}}^{(2)} = - \hat{M}_x H_1(t) \quad , \tag{2-29}$$

as the oscillating magnetic field is taken to be in the x-direction.

No truncation of M_x is needed for the case of equidistant unperturbed energy levels, and so in the absence of a crystalline electric field (and this includes the Ising model cases), $\hat{M}_x = M_x$. However, for non-equidistant energy levels, i.e. in the presence of a crystalline field, one must use

$$(\hat{M}_x)_{c.f.} = \left(\frac{3g}{2}\right) \sum_{\lambda \in G_1} \sum_i \left(S_{i\lambda}^{+} + S_{i\lambda+1}^{-} \right) \tag{2-30}$$

where $\sum_{\lambda \in G_1}$ means summation over all λ such that

$$\overline{T}_{\lambda+1} - \overline{T}_{\lambda} = \omega_0 \qquad (\lambda \in G_1) \quad , \tag{2-31}$$

and ω_0 is the unperturbed frequency of the primary line under consideration, not necessarily given by (2-14), but always positive.

It is of practical interest to know that $(\overline{\mathcal{H}})_{no\ c.f.}$ is a special case of $(\overline{\mathcal{H}})_{c.f.}$, and that $(\hat{M}_x)_{no\ c.f.}$ is a special case of $(\hat{M}_x)_{c.f.}$. To show this, one needs the help of the relations

$$\sum_{\lambda} S_{i\lambda}^{\mp} = S_i^{\mp} \tag{2-32}$$

$$\lambda \in G_1, \text{ all } \lambda \quad \text{(for no c.f.)} \tag{2-33}$$

$$(\lambda', \lambda'') \in G, \text{ all } \lambda', \lambda'' \quad \text{(for no c.f.)} \tag{2-34}$$

where in (2-34) it is assumed, naturally, that $\overline{I'_{\lambda+1}}$ and $\overline{I''_{\lambda+1}}$ exist (see equation (2-24)). (2-34) is a consequence of (2-33) and the definitions of the sets G and G_1. Equation (2-32) follows immediately from the definition (2-19) of the $\Delta^{\pm}_{i\lambda}$.

In developing our formalism for the line shape function, then, only the Hamiltonian describing the crystalline field case need be taken into consideration.

2. General Formalism of Absorption Line Shape.

We start from the well-known relation between the absorption constant $\sigma(\omega)$ and the magnetic susceptibility $\chi(\omega)$:

$$\sigma(\omega) = \text{const. } \omega \, \mathrm{Im}\, \chi(\omega), \quad (\omega > 0). \tag{2-35}$$

In the Kubo-type formulation (Kubo, 1957; O'Rourke, 1957) $\chi(\omega)$ is written as

$$\chi(\omega) = i \lim_{\varepsilon \to 0^+} \int_0^\infty dt \, e^{-i\omega t - \varepsilon t} \langle [M_x(t), \hat{M}_x] \rangle \tag{2-36}$$

where we have used the following notation:

M_x : the x-component of the total magnetization operator

$$O(t) \equiv e^{i\bar{\mathcal{H}}t} O e^{-i\bar{\mathcal{H}}t} \quad (\hbar = 1), \tag{2-37}$$

$\bar{\mathcal{H}}$ = will henceforth be called the Hamiltonian of the system

$$\langle \cdots \rangle = Q^{-1} \mathrm{Tr} \left(e^{-\bar{\mathcal{H}}/k_B T} \cdots \right), \quad Q = \mathrm{Tr} \left(e^{-\bar{\mathcal{H}}/k_B T} \right), \tag{2-38}$$

k_B : Boltzmann's constant,

T : temperature of the system at the time $t = -\infty$.

The following assumptions were involved in these formulas:

(1) The external magnetic field $\underline{H}_1(t)$ has been applied in the x-direction.

(2) The response is looked at in the x-direction.

(3) $\underline{H}_1(t)$ has been applied adiabatically starting from the distant past:

$$\lim \underline{H}_1(t) = 0.$$

(4) The system was in thermal equilibrium at $t = -\infty$.

(5) The Hamiltonian associated with the oscillating field is of the form

$$\hat{\mathcal{H}}^{(1)} = - \hat{\underline{M}} \cdot \underline{H}_1(t) \quad . \tag{2-39}$$

(6) The oscillating field is sufficiently weak that its effect can be treated in first order perturbation theory.

One normally defines the paramagnetic resonance line shape function to be not $\sigma(\omega)$, as given by (2-35), but $g(\omega)$ as given by

$$g(\omega) = \text{const.} \; \mathrm{Im}\, \chi(\omega) \,, \qquad (\omega > 0) \tag{2-35a}$$

where the constant is such that $g(\omega)$ is normalized to unity. (Cf. McMillan and Opechowski (1960)).

It is of advantage to keep only that part of $\chi(\omega)$ as defined by (2-36) which vanishes for $\omega < 0$. Employing equations (2-8), (2-9), (2-37), (2-30), (2-21), and (2-31), and the well-known identity

$$e^{-G} F e^{G} = \sum_{p=0}^{\infty} \frac{\{F, G\}^p}{p!} \tag{2-40}$$

where $\{F, G\}^p = \underbrace{[\ldots[F, G], G], \ldots G]}_{p \;\; G's}$, $\qquad \{F, G\}^0 = F$, $\tag{2-41}$

one has

$$\begin{aligned}
\hat{M}_x(-t) &= e^{-i\bar{\mathcal{H}}t} \hat{M}_x e^{i\bar{\mathcal{H}}t} = e^{-i(\mathcal{H}^{(0)} + \bar{\mathcal{H}}^{(1)})t} \hat{M}_x e^{i(\mathcal{H}^{(0)} + \bar{\mathcal{H}}^{(1)})t} \\
&= e^{-i\bar{\mathcal{H}}^{(1)}t} \left(e^{-i\mathcal{H}^{(0)}t} \hat{M}_x e^{i\mathcal{H}^{(0)}t}\right) e^{i\bar{\mathcal{H}}^{(1)}t} \\
&= \left(\frac{\beta g_\perp}{2}\right) e^{-i\bar{\mathcal{H}}^{(1)}t} \left[\sum_{\lambda \in G_1} \sum_i e^{-i\mathcal{H}^{(0)}t} \left(s_{i\lambda}^{+} + s_{i\lambda+1}^{-}\right) e^{i\mathcal{H}^{(0)}t}\right] e^{i\bar{\mathcal{H}}^{(1)}t} \\
&= \left(\frac{\beta g_\perp}{2}\right) e^{-i\bar{\mathcal{H}}^{(1)}t} \left[\sum_{\lambda \in G_1} \sum_i \left(e^{i\omega_0 t} s_{i\lambda}^{+} + e^{-i\omega_0 t} s_{i\lambda+1}^{-}\right)\right] e^{i\bar{\mathcal{H}}^{(1)}t}
\end{aligned} \tag{2-42}$$

With the use of the identity (2-43) which follows from the cyclic properties of the trace for any operators A and B

$$\langle [A, B(t)] \rangle = \langle [A(-t), B] \rangle \tag{2-43}$$

and the relation

$$M_{xc} = \frac{\beta g_\perp}{2} \sum_j (S_j^+ + S_j^-) \tag{2-44}$$

equation (2-36) can be rewritten as follows:

$$\begin{aligned}
\chi(\omega) = & \frac{i}{4} \lim_{\varepsilon \to 0^+} \int_0^\infty dt\, e^{-i(\omega-\omega_0)t-\varepsilon t} (\beta g_\perp)^2 \sum_i \sum_j \sum_{\lambda \in G_1} \langle [S_j^+, e^{-i\bar{\mathcal{H}}^{(1)}t} S_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t}] \rangle \\
& + \frac{i}{4} \lim_{\varepsilon \to 0^+} \int_0^\infty dt\, e^{-i(\omega-\omega_0)t-\varepsilon t} (\beta g_\perp)^2 \sum_i \sum_j \sum_{\lambda \in G_1} \langle [S_j^-, e^{-i\bar{\mathcal{H}}^{(1)}t} S_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t}] \rangle \\
& + \frac{i}{4} \lim_{\varepsilon \to 0^+} \int_0^\infty dt\, e^{-i(\omega+\omega_0)t-\varepsilon t} (\beta g_\perp)^2 \sum_i \sum_j \sum_{\lambda \in G_1} \langle [S_j^+, e^{-i\bar{\mathcal{H}}^{(1)}t} S_{i\lambda+1}^- e^{i\bar{\mathcal{H}}^{(1)}t}] \rangle \\
& + \frac{i}{4} \lim_{\varepsilon \to 0^+} \int_0^\infty dt\, e^{-i(\omega+\omega_0)t-\varepsilon t} (\beta g_\perp)^2 \sum_i \sum_j \sum_{\lambda \in G_1} \left\{ \langle [S_j^-, e^{-i\bar{\mathcal{H}}^{(1)}t} S_{i\lambda+1}^- e^{i\bar{\mathcal{H}}^{(1)}t}] \rangle \right\}
\end{aligned} \tag{2-45}$$

First, notice that in the second integral, $S_j^- = \sum_\lambda A_{j\lambda+1}^-$ may be replaced by $\sum_{\lambda' \in G_1} A_{j\lambda'+1}^-$ (see Appendix I).

As the system is definitely quantized along the z-axis, the first and fourth integrals vanish automatically. Moreover, the third integral provides a negligible contribution to $\chi(\omega)$ for $\omega > 0$; this follows from the weak-interaction assumption:(2-3) if one puts $\bar{\mathcal{H}}^{(1)} = 0$, the integral gives a delta-function peak at $\omega = -\omega_0$. Inclusion of $\bar{\mathcal{H}}^{(1)}$ serves to introduce many other delta-function peaks into the region around $-\omega_0$, with very little overlap into the region of positive ω. By a similar argument, the second integral is seen to provide a negligible contribution to $\chi(\omega)$ in the region of negative ω.#

This argument is equivalent to that of McMillan and Opechowski (1960). They argue that if $\bar{\mathcal{H}}^{(1)}$ is not too large, $E_\alpha < E_\beta$ implies $E_{\alpha,i} < E_{\beta,k}$ except for a negligible number of pairs of states $|\alpha,i\rangle, |\beta,k\rangle$ where $\bar{\mathcal{H}}^{(1)}|\mu,k\rangle = E_{\mu,k}|\mu,k\rangle$ and $\mathcal{H}|\mu,k\rangle = E_{\mu,k}|\mu,k\rangle$ ($k = 1,2,\ldots,g_\mu$, the degeneracy of E_μ).

Thus, if the magnetic susceptibility is redefined in terms of the second integral alone, i.e.

$$\chi(\omega) = \frac{i(\beta g_\perp)^2}{4} \lim_{\varepsilon \to 0^+} \int_0^\infty dt\, e^{-i\omega t - \varepsilon t} \left\langle \left[\sum_j \sum_{\lambda \in G_1} S_{j\lambda+1}^-(t), \sum_i \sum_{\lambda \in G_1} S_{i\lambda}^+ \right] \right\rangle \tag{2-46}$$

then (2-35) may be rewritten without the condition " $\omega > 0$ ". Further, one always has

$$\int_0^\infty \psi(\omega)\, \chi(\omega)\, d\omega = \int_{-\infty}^\infty \psi(\omega)\, \chi(\omega)\, d\omega \tag{2-47}$$

where $\psi(\omega)$ is any function of ω .

The function $\chi(\omega)$ as given by (2-46) is closely related to the temperature-dependent double-time Green's function. These Green's functions were first introduced by Bogoliubov et al. (Bogoliubov and Tyablikov, 1959; Zubarev, 1960). The Green's function $\ll A \mid B \gg_E$ of the operators A and B is a two-branch analytic function of E defined everywhere outside the real axis by

$$\ll A \mid B \gg_E \begin{cases} = i/2\pi \int_{-\infty}^0 dt\, e^{iEt} \langle [A(t), B] \rangle \; ; \; \mathrm{Im}\, E < 0 \\ = -i/2\pi \int_0^\infty dt\, e^{iEt} \langle [A(t), B] \rangle \; ; \; \mathrm{Im}\, E > 0 \end{cases} \tag{2-48}$$

By comparison of (2-46) with (2-48) one can immediately see the relation

$$\chi(\omega) = -\frac{2\pi}{4} (\beta g_\perp)^2 \lim_{\varepsilon \to 0^+} \ll \sum_j \sum_{\lambda' \in G_1} S_{j\lambda'+1}^- \mid \sum_i \sum_{\lambda \in G_1} S_{i\lambda}^+ \gg_{-\omega + i\varepsilon} \tag{2-49}$$

$$= -\frac{2\pi}{4} (\beta g_\perp)^2 \lim_{\varepsilon \to 0^+} \ll \sum_i \sum_{\lambda \in G_1} S_{i\lambda}^+ \mid \sum_j \sum_{\lambda' \in G_1} S_{j\lambda'+1}^- \gg_{\omega - i\varepsilon}$$

where we have used only the identity (2-43).

Note that the above Green's function is of the form $\ll A \mid A^* \gg_E$ (by (2-25)).

One can show that the Green's function $\ll A \mid B \gg_E$ as defined by (2-48) is analytic both in the upper and lower half-planes and that it is found from the hierarchy of equations

$$\begin{aligned} E \ll A \mid B \gg_E &= \frac{1}{2\pi} \langle [A, B] \rangle + \ll [A, \mathcal{H}] \mid B \gg_E \\ E \ll [A, \mathcal{H}] \mid B \gg_E &= \frac{1}{2\pi} \langle [[A, \mathcal{H}], B] \rangle + \ll [[A, \mathcal{H}], \mathcal{H}] \mid B \gg_E \\ &\vdots \qquad\qquad \vdots \qquad\qquad \vdots \end{aligned} \tag{2-50}$$

Our problem is then to solve this hierarchy with the condition that the solution be analytic in the domain for which the Green's function is defined, that is, outside the real axis. The actual procedure of solving this equation approximately will be discussed in Chapter V. For further details of the Green's function method, we refer to Zubarev's article.

CHAPTER III

Green's Functions and the Ising Model#

In some simple cases it is found that the hierarchy of Green's Function equations (2-50) decouples automatically after a finite number of steps. One such case is the problem of finding the amplitudes and frequencies of the three component lines in the absorption band of the one-dimensional Ising model, consisting of an arbitrary number N of identical spins arranged in a ring. It is assumed that each spin has spin quantum number ½, and that only nearest-neighbour interactions occur.

The Hamiltonian of this system is given by equations (2-26), (2-27), and (2-28), i.e.

$$\bar{\mathcal{H}} = -h \sum_{\ell=1}^{N} S_\ell^z - \epsilon \sum_{k=1}^{N} S_k^z S_{k+1}^z \qquad (3\text{-}1)$$

where

$h = \omega_0$ as given by equation (2-14)

$\epsilon =$ exchange interaction constant

ℓ and k label the lattice sites, with the $(N+1)^{st}$ site identical with the 1st.

The line shape function $g(\omega)$ is again defined by equation (2-35a), which, through equation (2-49) specialized to the no-crystalline field case, leads to

$$g(\omega) \propto \lim_{\varepsilon \to 0^+} \mathrm{Im}\, G_0 |_{\omega - i\varepsilon} \qquad (3\text{-}2)$$

I am indebted to Professor W. Opechowski for his suggestion that this problem be considered.

where

$$G_{0|E} \equiv \sum_{\ell} \sum_{p} \langle\langle S_{\ell}^{+} | S_{p}^{-} \rangle\rangle_{E} \tag{3-3}$$

The first three Green's function equations are then

$$(E-h)\langle\langle S_{\ell}^{+} | S_{p}^{-} \rangle\rangle_{E} = \frac{1}{2\pi} \cdot 2 \langle S_{\ell}^{z} \rangle \delta_{\ell p} + \epsilon \langle\langle S_{\ell}^{+} (S_{\ell-1}^{z} + S_{\ell+1}^{z}) | S_{p}^{-} \rangle\rangle_{E} \tag{3-4}$$

$$(E-h)\langle\langle S_{\ell}^{+} (S_{\ell-1}^{z} + S_{\ell+1}^{z}) | S_{p}^{-} \rangle\rangle_{E} = \frac{1}{2\pi} \cdot 4 \langle S_{\ell}^{z} S_{\ell+1}^{z} \rangle \delta_{\ell p} + \epsilon \langle\langle S_{\ell}^{+} (S_{\ell-1}^{z} + S_{\ell+1}^{z})^{2} | S_{p}^{-} \rangle\rangle_{E} \tag{3-5}$$

$$\begin{aligned}(E-h)\langle\langle S_{\ell}^{+} (S_{\ell-1}^{z} + S_{\ell+1}^{z})^{2} | S_{p}^{-} \rangle\rangle_{E} &= \frac{1}{2\pi} \langle S_{\ell}^{z} \rangle \delta_{\ell p} + \frac{1}{2\pi} \cdot 4 \langle S_{\ell-1}^{z} S_{\ell}^{z} S_{\ell+1}^{z} \rangle \delta_{\ell p} \\ &\quad + \epsilon \langle\langle S_{\ell}^{+} (S_{\ell-1}^{z} + S_{\ell+1}^{z})^{3} | S_{p}^{-} \rangle\rangle_{E} \\ &= \frac{1}{2\pi} \delta_{\ell p} \left(\langle S_{\ell}^{z} \rangle + 4 \langle S_{\ell-1}^{z} S_{\ell}^{z} S_{\ell+1}^{z} \rangle \right) \\ &\quad + \epsilon \langle\langle S_{\ell}^{+} (S_{\ell-1}^{z} + S_{\ell+1}^{z}) | S_{p}^{-} \rangle\rangle_{E}\end{aligned} \tag{3-6}$$

The last term in equation (3-6) arises since

$$(S_{\ell-1}^{z} + S_{\ell+1}^{z})^{3} = (S_{\ell-1}^{z} + S_{\ell+1}^{z}) \tag{3-7}$$

is a consequence of the relation

$$(S_{\ell}^{z})^{2} = 1/4 , \qquad (S = 1/2) . \tag{3-8}$$

It is now seen that equations (3-4), (3-5), and (3-6) form a closed set of simultaneous equations which can easily be solved for $G_{0|E}$; that is, there is no need to write any higher-order equations. Since this state of affairs appeared without any decoupling becoming necessary, we say that the hierarchy decouples automatically at the third stage. The solution is

$$\ll S_e^+ | S_p^- \gg_E = \frac{\delta_{ep}}{2\pi} \left\{ \frac{1}{e} \left(\langle 1 \rangle - 4\langle 3 \rangle \right) + \frac{1}{2(e+\epsilon)} \left(\langle 1 \rangle - 4\langle 2 \rangle + 4\langle 3 \rangle \right) \right.$$
$$\left. + \frac{1}{2(e-\epsilon)} \left(\langle 1 \rangle + 4\langle 2 \rangle + 4\langle 3 \rangle \right) \right\} \tag{3-9}$$

where we have introduced the notation

$$\begin{aligned} e &= E - h \\ \langle 1 \rangle &= \langle S_i^z \rangle \\ \langle 2 \rangle &= \langle S_i^z S_{i+1}^z \rangle \\ \langle 3 \rangle &= \langle S_{i-1}^z S_i^z S_{i+1}^z \rangle \end{aligned} \tag{3-10}$$

noting that $\langle 1 \rangle$, $\langle 2 \rangle$, and $\langle 3 \rangle$ are independent of i because of translational invariance.

The line shape is then given, with the use of (3-2) and (3-3), by

$$\begin{aligned} g_{\text{norm.}}(\omega) &= \lim_{\epsilon \to 0^+} \operatorname{Im} G_{0\,\text{norm.}} \Big|_{E = \omega - i\epsilon} \\ &= \frac{1}{2\langle 1 \rangle} \left[\left(\langle 1 \rangle - 4\langle 3 \rangle \right) \delta(\omega - h) \right. \\ &+ \left(\tfrac{1}{2}\langle 1 \rangle - 2\langle 2 \rangle + 2\langle 3 \rangle \right) \delta(\omega - h + \epsilon) \\ &\left. + \left(\tfrac{1}{2}\langle 1 \rangle + 2\langle 2 \rangle + 2\langle 3 \rangle \right) \delta(\omega - h - \epsilon) \right] \end{aligned} \tag{3-11}$$

which is a sum of three delta-functions at specified frequencies, with amplitudes given by linear combinations of thermal averages.

It now remains to calculate these thermal averages. Since several authors (e.g. Huang, 1963) have derived explicit representations for the partition function Z, we will take it that Z is known, and use Huang's result

$$Z = (\lambda_+)^N + (\lambda_-)^N \tag{3-12}$$

where

$$\lambda_{\pm} = e^{\beta\epsilon/4}\left[\cosh\left(\tfrac{1}{2}\beta h\right) \pm \sqrt{\cosh^2\left(\tfrac{1}{2}\beta h\right) - 2e^{-\frac{\beta\epsilon}{2}}\sinh\left(\tfrac{1}{2}\beta\epsilon\right)}\right] \quad (3\text{-}12)$$

We immediately get $\langle 1\rangle$ and $\langle 2\rangle$ by direct differentiation from the formulas

$$\langle 1\rangle = \frac{1}{NZ}\frac{\partial}{\partial(\beta h)}Z \quad (3\text{-}14)$$

$$\langle 2\rangle = \frac{1}{NZ}\frac{\partial Z}{\partial(\beta\epsilon)} \quad (3\text{-}15)$$

The thermal average $\langle 3\rangle$ is obtained as a linear combination of $\langle 1\rangle$ and $\langle 2\rangle$ by the use of the following general identity (see, e.g., Zubarev, 1960)

$$\langle B(t)A(t')\rangle = i\int_{-\infty}^{\infty} d\omega\, e^{-i\omega(t-t')}\frac{\{\langle\langle A|B\rangle\rangle_{\omega+i\varepsilon} - \langle\langle A|B\rangle\rangle_{\omega-i\varepsilon}\}}{e^{\beta\omega}-1} \quad (3\text{-}16)$$

Putting $t = t' = 0$, $A = S_i^+$, and $B = S_i^-$ in equation (3-16), and using the result (3-9), we get

$$\frac{1}{2} - \langle 1\rangle = \frac{\langle 1\rangle - 4\langle 3\rangle}{e^{\beta h}-1} + \frac{\frac{1}{2}(\langle 1\rangle - 4\langle 2\rangle + 4\langle 3\rangle)}{e^{\beta(h-\epsilon)}-1} + \frac{\frac{1}{2}(\langle 1\rangle + 4\langle 2\rangle + 4\langle 3\rangle)}{e^{\beta(h+\epsilon)}-1} \quad (3\text{-}17)$$

or,

$$\langle 3\rangle = D_0 + D_1\langle 1\rangle + D_2\langle 2\rangle \quad (3\text{-}18)$$

where D_0, D_1, and D_2 are simple functions of h and ϵ. In the derivation of (3-17), use was made of the relation

$$S_i^- S_i^+ = \frac{1}{2} - S_i^z, \quad (S = 1/2) \quad (3\text{-}19)$$

Equations (3-14), (3-15), and (3-18), when combined with equations (3-12), (3-13), and (3-17), give us, when substituted into equation (3-11), an explicit representation of the absorption band of the one-dimensional Ising model. The result corresponds exactly with that found by Y.Y. Lee (1961), who had quite complicated summations to perform. The latter arose from his combinatorial approach to the problem, and necessitated the finding of suitable generating functions. He simplified the combinatorial problem by specializing to the case in which $N = 4P - 1$ ($P=1,2,...$) and then considered his results valid for large N. In our approach there is no need for this specialization, as the complicated combinatorial problem is avoided. The advantage of our method lies in the identification of the amplitudes of the resonance lines with easily recognizable thermal averages, and in the ease with which these averages can be calculated, from a knowledge of the partition function, through differentiation and further application of the Green's function technique.

The thermal average $\langle 3 \rangle$ cannot be obtained directly from Z; nor can higher-order thermal averages. A direct method of finding thermal averages, using difference equations, is given in Appendix II.

CHAPTER IV

The Moment Method

1. General Discussion

In the problem of the general paramagnetic resonance line shape, unlike that of the one-dimensional Ising Model, the hierarchy of Green's function equations (2-50) does not decouple automatically at an early stage. The solution of this problem by the Green's function technique then involves looking for a decoupling procedure which gives a closed set of equations satisfying the following requirements: it must be (a) simple enough to be tractable, (b) complicated enough to yield far more than the small number of isolated delta-function peaks obtained for the Ising model, and (c) "faithful" enough so that it furnishes a line shape function that is resonably close, in some approximation at least, to the experimentally-observed line shape.

The difficulties inherent in the search for such a suitable decoupling procedure are representative of those encountered in other approaches to the line shape problem. Consequently, a method has been evolved which enables one to discuss the shape of the resonance lines without actually having to find an analytic expression for the line shape function. Known as the "moment method", this procedure consists in defining a line shape function in a formal way, and in calculating its first few moments in various approximations. It was introduced by Van Vleck (1948), and used by Pryce and Stevens (1950), Kambe and Usui (1952) and McMillan and Opechowski (1960). Kambe and Usui derived quite general exact expressions for the moments, and these were applied by McMillan and Opechowski to the case in which a crystalline electrostatic field is present. In this

section, a derivation, different from that of Kambe and Usui, of the expressions for the moments is given.

We shall show that if a normalized line shape function $g_{BA}(\omega)$, defined by

$$g_{BA}(\omega) = \mathrm{Im}\ \chi_{BA}(\omega) \Big/ \int_0^\infty \mathrm{Im}\ \chi_{BA}(\omega)\, d\omega \tag{4-1}$$

with

$$\chi_{BA}(\omega) = \lim_{\varepsilon \to 0^+} -i \int_0^\infty dt\, e^{-i(\omega - i\varepsilon)t} \langle [A, B(t)] \rangle \tag{4-2}$$

satisfies the conditions that

$$A^* = B \tag{4-3}$$

and that

$$g_{BA}(\omega) = 0 \quad , \omega < 0 \ , \tag{4-4}$$

then its p^{th} moment about the origin, μ_p , is given by

$$\mu_p = \langle [\{A, \bar{\mathcal{H}}\}^p, B] \rangle \Big/ \langle [A, B] \rangle \qquad p=0,1,2,\ldots \tag{4-5}$$

With the use of (2-40), (2-43), (4-3), and the identity

$$\langle [A(t), B] \rangle^* = \langle [B^*, A^*(t)] \rangle \tag{4-6}$$

we can immediately write, from (4-2),

$$\begin{aligned} \mathrm{Im}\ \chi_{BA}(\omega) &= (1/2i)\left(\chi_{BA}(\omega) - \chi^*_{BA}(\omega)\right) \\ &= \lim_{\varepsilon \to 0^+} -\tfrac{1}{2} \int_{-\infty}^{\infty} dt\, e^{-i\omega t - \varepsilon |t|} \langle [A(-t), B] \rangle \\ &= \lim_{\varepsilon \to 0^+} -\tfrac{1}{2} \int_{-\infty}^{\infty} dt\, e^{-i\omega t - \varepsilon |t|} \sum_{p=0}^{\infty} \frac{(it)^p}{p!} \langle [\{A, \bar{\mathcal{H}}\}^p, B] \rangle \end{aligned} \tag{4-7}$$

We now make use of the characteristic function M(t), defined by

$$M(t) = \int_{-\infty}^{\infty} d\omega \; e^{i\omega t} g_{BA}(\omega) \tag{4-8}$$

which possesses the inverse Fourier transform

$$g_{BA}(\omega) = 2\pi \int_{-\infty}^{\infty} dt \; e^{-i\omega t} M(t) \tag{4-9}$$

Repeated differentiation of (4-8) with respect to t, i.e.

$$\frac{d^p}{dt^p} M(t)\Big|_{t=0} = i^p \int_{-\infty}^{\infty} d\omega \; \omega^p g_{BA}(\omega) \equiv i^p \mu_p \tag{4-10}$$

gives, simply, the Taylor coefficients in the expansion of M(t) about t=0, i.e.

$$M(t) = \sum_{p=0}^{\infty} \frac{(it)^p}{p!} \mu_p \tag{4-11}$$

Substituting from (4-11) into (4-9), we get

$$g_{BA}(\omega) = 2\pi \int_{-\infty}^{\infty} dt \; e^{-i\omega t} \sum_{p=0}^{\infty} \frac{(it)^p}{p!} \mu_p \tag{4-12}$$

Comparison of (4-12) with the alternate expression for $g_{BA}(\omega)$ given by (4-1) and (4-7) yields

$$\mu_p = (\text{constant, independent of p}) \times \langle [\{A, \bar{\mathcal{H}}\}^p, B] \rangle \tag{4-13}$$

The constant is determined by the normalization requirement on $g_{BA}(\omega)$, resulting in the required expression, (4-5), for the moments about the origin.

If, further, $\bar{\mathcal{H}}$ can be expressed according to (2-9) as

$$\bar{\mathcal{H}} = \mathcal{H}^{(0)} + \bar{\mathcal{H}}^{(1)}$$

where (2-10) holds, and also

$$[A, \mathcal{H}^{(0)}] = \omega_0 A \tag{4-14}$$

then

$$M_p \equiv \int (\omega - \omega_0)^p g_{BA}(\omega) d\omega = \frac{\langle [\{A, \bar{\mathcal{H}}^{(1)}\}^p, B] \rangle}{\langle [A, B] \rangle} \tag{4-15}$$

are the moments about the unperturbed frequency ω_0. (We call the M_p "central moments".)

For

$$\mu_p = \int \omega^p g_{BA}(\omega) d\omega = \int (\omega - \omega_0 + \omega_0)^p g_{BA}(\omega) d\omega$$

$$= \int \sum_{r=0}^{p} {}^pC_r (\omega - \omega_0)^r \omega_0^{p-r} g_{BA}(\omega) d\omega$$

$$= \sum_{r=0}^{p} {}^pC_r \omega_0^{p-r} M_r \tag{4-16}$$

Also, by induction it can be shown, using (4-14) and (2-10), that

$$\{A, \bar{\mathcal{H}}\}^p = \sum_{r=0}^{p} {}^pC_r \omega_0^{p-r} \{A, \bar{\mathcal{H}}^{(1)}\}^r \tag{4-17}$$

Combining with (4-5), we get

$$\sum_{r=0}^{p} {}^pC_r \omega_0^{p-r} M_r = \sum_{q=0}^{p} {}^pC_q \omega_0^{p-q} \frac{\langle [\{A, \bar{\mathcal{H}}^{(1)}\}^q, B] \rangle}{\langle [A, B] \rangle} \tag{4-18}$$

Taking p=0,1,2,... successively, we see that formula (4-15) follows.

2. Application to Paramagnetic Resonance Line Shape Problem.

For the paramagnetic resonance line shape problem, one can immediately proceed to calculate moments in various approximations by substituting

$$A = \sum_i \sum_{\lambda \in G_1} A_{i\lambda}^{+} \tag{4-19}$$

and

$$B = A^{+} = \sum_j \sum_{\lambda' \in G_1} A_{j\lambda'}^{-} \tag{4-20}$$

into the expressions (4-15) for the central moments. The expressions (4-19) and (4-20) for A and B come from equation (2-46) for $\chi(\omega)$. One takes commutators with $\bar{\mathcal{H}}^{(1)}$ (equation (2-23)) according to the rules (2-20) and (2-22), and takes traces in the most convenient representation. This procedure is straightforward.

McMillan and Opechowski (1960), starting from formulas first derived by Kambe and Usui, were able to cast expressions for the first and second central moments into a form suitable for computation. They then applied their results to the specialized problem that we have been considering. Their only initial assumptions are given by our inequalities (2-3) and (2-4). The procedure for their calculation of the first central moment, M_1, will here be given in outline. They start with

$$M_1 = \frac{\frac{1}{2} \mathrm{Tr}\left(b^{\bar{\mathcal{H}}} [\hat{M}, [\bar{\mathcal{H}}^{(1)}, \hat{M}]]\right)}{\mathrm{Tr}\left(b^{\bar{\mathcal{H}}} [\hat{M}_-, \hat{M}_+]\right)} \tag{4-21}$$

where

$$b^{\mathcal{H}} = \exp(-\mathcal{H}/k_B T)$$

$\hat{M} = \hat{M}_+ + \hat{M}_-$ is the component of the magnetic moment of the spin system in the direction of the oscillating field, truncated so as to single out a particular primary line.

$\hat{M}_+$ and $\hat{M}_-$ are defined by

$$(\alpha,i|\hat{M}_+|\beta,k) = \begin{cases} (\alpha,i|M|\beta,k) & \text{if } |E_\alpha - E_\beta| = \omega_0 \text{ and } E_{\alpha,i} > E_{\beta,k} \\ 0 & \text{otherwise} \end{cases} \tag{4-22}$$

$$(\alpha,i|\hat{M}_-|\beta,k) = \begin{cases} (\alpha,i|M|\beta,k) & \text{if } |E_\beta - E_\alpha| = \omega_0 \text{ and } E_{\beta,k} > E_{\alpha,i} \\ 0 & \text{otherwise} \end{cases} \tag{4-23}$$

where $|\alpha,i)$ satisfies the eigenvalue equations

$$\mathcal{H}^{(0)}|\alpha,i) = E_\alpha|\alpha,i), \quad (i = 1,2,\ldots,g_\alpha, \text{ the degeneracy of } E_\alpha) \tag{4-24}$$

$$\bar{\mathcal{H}}|\alpha,i) = E_{\alpha,i}|\alpha,i) \tag{4-25}$$

They then rewrite equation (4-21) in terms of $\mathcal{H}$ and M rather than $\bar{\mathcal{H}}$, $\hat{M}$, $\hat{M}_+$ and $\hat{M}_-$. This is done with the use of projection operators P_λ defined such that

$$P_\lambda|\mu,k) = \delta_{\lambda\mu}|\lambda,k) \tag{4-26}$$

With the use of the observation that if $\bar{\mathcal{H}}^{(1)}$ is not too large, then $E_\alpha < E_\beta$ implies $E_{\alpha,i} < E_{\beta,k}$ except for a negligible number of pairs of states $|\alpha,i)$, $|\beta,k)$, the definitions (4-22) and (4-23) of $\hat{M}_+$ and $\hat{M}_-$ are changed to

$$(\alpha,i|\hat{M}_+|\beta,k) = \begin{cases} (\alpha,i|M|\beta,k) & \text{if } E_\alpha - E_\beta = \omega_0 \\ 0 & \text{otherwise} \end{cases} \tag{4-27}$$

$$(\alpha,i|\hat{M}_-|\beta,k) = \begin{cases} (\alpha,i|M|\beta,k) & \text{if } E_\beta - E_\alpha = \omega_0 \\ 0 & \text{otherwise} \end{cases} \tag{4-28}$$

Then

$$\bar{\mathcal{H}} = \sum_\mu P_\mu \mathcal{H} P_\mu \tag{4-29}$$

$$\hat{M}_+ = \sum_{\alpha,\beta} P_\beta M P_\alpha \tag{4-30}$$

$$\hat{M}_- = \sum_{\alpha,\beta} P_\alpha M P_\beta \tag{4-31}$$

where $\sum_{\alpha,\beta}$ means summation over all values of α and β wherein

$$E_\beta - E_\alpha = \omega_0 \quad . \tag{4-32}$$

Equation (4-21) becomes

$$M_1 = C^{(1)} / B \tag{4-33}$$

where

$$B = \sum_{\alpha,\beta} Tr \left\{ b^{P_\alpha \mathcal{H} P_\alpha} P_\alpha M P_\beta M - b^{P_\beta \mathcal{H} P_\beta} P_\beta M P_\alpha M \right\} \tag{4-34}$$

$$C^{(1)} = \sum_{\alpha,\beta} Tr \left\{ b^{P_\alpha \mathcal{H} P_\alpha} \left(P_\alpha M P_\beta \mathcal{H}^{(1)} P_\beta M - P_\alpha \mathcal{H}^{(1)} P_\alpha M P_\beta M \right) \right. \tag{4-35}$$
$$\left. - b^{P_\beta \mathcal{H} P_\beta} \left(P_\beta \mathcal{H}^{(1)} P_\beta M P_\alpha M - P_\beta M P_\alpha \mathcal{H}^{(1)} P_\alpha M \right) \right\} .$$

McMillan and Opechowski make use of an approximation technique used by Pryce and Stevens, and also by Kambe and Usui. This technique depends on the weak-interaction assumption (2-3). One expands all exponentials involving $\bar{\mathcal{H}} = \mathcal{H}^{(0)} + \bar{\mathcal{H}}^{(1)}$ as follows

$$e^{C_1 \bar{\mathcal{H}} C_2} = e^{C_1 \mathcal{H}^{(0)} C_2} \left[1 + C_1 \bar{\mathcal{H}}^{(1)} C_2 + \frac{1}{2!} \left(C_1 \bar{\mathcal{H}}^{(1)} C_2 \right)^2 + \cdots \right]$$

provided $\left[C_1 \mathcal{H}^{(0)} C_2 , C_1 \bar{\mathcal{H}}^{(1)} C_2 \right] = 0$, and keeps only the lowest-order terms in the square brackets. Here C_1 and C_2 are any operators such that the above provision is satisfied. We call the approximation which consists in keeping only the first ℓ terms in the brackets, the "ℓ^{th} approximation of McMillan and Opechowski", and denote it by $(MO)_\ell$.

Evaluation of formula (4-33) in $(MO)_1$ consists then in replacing $b^{P_\alpha \mathcal{H} P_\alpha}$ by $b^{E_\alpha P_\alpha}$. The analysis is done by McMillan and Opechowski for the case when the unperturbed spin has R energy values $a_1, a_2, a_3, \ldots, a_R$ (the equivalent of our T_λ) which are all non-degenerate. In this connection, a set G_2 is defined such that if τ is in G_2 , there exists an integer τ' such that

$$a_{\tau'} - a_\tau = w_0 \tag{4-36}$$

In the first approximation the term B (4-34) can then easily be reduced to the form

$$B = (1 - b^{w_0}) \sum_{\alpha,\beta} b^{E_\alpha} \sum_{i=1}^{g_\alpha} \sum_{k=1}^{g_\beta} \left| (\alpha, i | M | \beta, k) \right|^2 . \tag{4-37}$$

In the above form, the calculation of B becomes a combinatorial problem, and involves doing summations like

$$\sum_{\substack{n_1 + n_2 + \cdots + n_R = N \\ (0 \le n_i \le N)}} b^{(n_1 a_1 + n_2 a_2 + \cdots + n_R a_R)} \times \sum_{\tau \in G_2} \frac{\left| \sum_j (\tau' | M_j | \tau)_j \right|^2 (N-1)!}{n_1! \, n_2! \cdots (n_\tau - 1)! \cdots n_R!} \tag{4-38}$$

where $|\tau)_i$ are the unperturbed eigenfunctions of the i^{th} spin, with eigenvalues a_τ so that

$$\mathcal{H}_i^{(0)} |r)_i = a_r |r)_i \qquad , \qquad \begin{matrix} i = 1, 2, \ldots, N \\ r = 1, 2, \ldots, R \end{matrix} \quad . \tag{4-39}$$

The cause of the combinatorial problem is in the degeneracy of the E_α .

The degree of complexity increases when expressions like $C^{(1)}$ and those entering the higher moments are considered, and when approximations higher than the first are used.

The combinatorial problem is avoided for the special case that we consider by the introduction of the operators $\mathcal{A}_{i\lambda}^{\pm}$ defined by (2-19). To see how these operators simplify the calculations for our special case, we show how the more general case of McMillan and Opechowski is simplified by the use of a different kind of projection operator; these projection operators, first introduced by Kambe and Usui (1952), are then related, for the special case, to the operators $\mathcal{A}_{i\lambda}^{\pm}$.

We define projection operators P_λ^i which project onto eigenstates of $\mathcal{H}_i^{(0)}$, rather than the operators P_λ which project onto eigenstates of the full Zeeman Hamiltonian, by

$$P_\lambda^i |\lambda'')_i = \delta_{\lambda\lambda''} |\lambda)_i \quad . \tag{4-40}$$

The relations

$$P_\lambda^i P_{\lambda''}^i = \delta_{\lambda\lambda''} P_\lambda^i \tag{4-41}$$

and

$$\left[P_\lambda^i , \mathcal{H}_i^{(0)} \right] = 0 \tag{4-42}$$

follow from the definition (4-40).

Note that in these equations λ no longer labels eigenvalues of S_i^z, but only eigenvalues of $\mathcal{H}_i^{(0)}$ according to equation (4-39).

One can then show that the following expressions for $\hat{M}_+$ and $\hat{M}_-$ satisfy the definitions (4-27) and (4-28):

$$\hat{M}_+ = \sum_i \sum_{\lambda \in G_2} P_{\lambda'}^i M_i P_\lambda^i \tag{4-43}$$

$$\hat{M}_- = \sum_i \sum_{\lambda \in G_2} P_\lambda^i M_i P_{\lambda'}^i \tag{4-44}$$

where $$M = \sum_{i=1}^{N} M_i \tag{4-45}$$

One also has

$$\overline{\mathcal{H}_{ij}^{(1)}} = \sum_{\lambda_1} \sum_{\lambda_2} \sum_{\lambda_3 \lambda_4} P_{\lambda_1}^i P_{\lambda_2}^j \mathcal{H}_{ij}^{(1)} P_{\lambda_3}^j P_{\lambda_4}^i \tag{4-46}$$

where $\sum_{\lambda_3 \lambda_4}$ means summation over all λ_3, λ_4 such that

$$a_{\lambda_3} + a_{\lambda_4} = a_{\lambda_1} + a_{\lambda_2} \tag{4-47}$$

One can prove the above statements by considering matrix elements of $\hat{M}_+$, $\hat{M}_-$, and $\overline{\mathcal{H}^{(1)}}$ (as given above) between the orthonormal product eigenstates

$$|\lambda_1 \lambda_2 \lambda_3 \ldots \lambda_N) = |\lambda_1)_1 \times |\lambda_2)_2 \times |\lambda_3)_3 \times \ldots \times |\lambda_N)_N \tag{4-48}$$

Here $|\lambda_1)_1$, for example, is an eigenstate of $\mathcal{H}_1^{(0)}$ with eigenvalue a_{λ_1}. The product eigenstates (4-48) are themselves eigenstates of $\mathcal{H}^{(0)} = \sum_i \mathcal{H}_i^{(0)}$ with eigenvalues $a_{\lambda_1} + a_{\lambda_2} + \ldots + a_{\lambda_N} = E_\mu$, and are linear combinations of the $|\mu, i)$ defined by (4-24) and (4-25), for fixed μ.

Let us now evaluate

$$B = \overline{\mathrm{Tr}} \left(b^{\mathcal{H}^{(0)}} [\hat{M}_-, \hat{M}_+] \right), \tag{4-49}$$

the first approximation part of the denominator of M_1 given by equation (4-33), with the use of the P_λ^i . Using (4-43) and (4-44),

$$B = \sum_{r\in G_2} \sum_{s\in G_2} \sum_i \sum_j Tr\left(b^{\sum_\ell \mathcal{H}_\ell^{(0)}} [P_r^i M_i P_{r'}^i, P_{s'}^j M_j P_s^j]\right) \tag{4-50}$$

From (4-41) and translational invariance,

$$B = N \sum_{r\in G_2} Tr\left\{b^{\sum_\ell \mathcal{H}_\ell^{(0)}} \left(P_r^i M_i P_{r'}^i M_i P_r^i - P_{r'}^i M_i P_r^i M_i P_{r'}^i\right)\right\} \tag{4-51}$$

Let us consider only the first term of (4-51), and expand the trace in the orthonormal product eigenstates (4-48).

$$\begin{aligned} B\ (1^{st}\ term) &= N \sum_{r\in G_2} \sum_{\lambda_1,\lambda_2,\ldots,\lambda_N} \left\{ (\lambda_N \lambda_{N-1} \ldots \lambda_1 | \prod_\ell b^{\mathcal{H}_\ell^{(0)}} \right. \\ &\quad \left. \times (P_r^i M_i P_{r'}^i M_i P_r^i) | \lambda_1, \lambda_2, \ldots, \lambda_N) \right\} \\ &= N \sum_{r\in G_2} \left\{ \sum_{\substack{\lambda_1,\ldots\lambda_\rho\ldots\lambda_N \\ (\lambda_\rho \neq \lambda_i)}} \prod_\ell b^{a_{\lambda_\ell}} \right\} \sum_{\lambda_i} (\lambda_i | b^{\mathcal{H}_i^{(0)}} P_r^i M_i P_{r'}^i M_i P_r^i | \lambda_i) \\ &= N \sum_{r\in G_2} \left\{ Z^{N-1} \right\} b^{a_r} \left| \sum_i (r | M_i | r')_i \right|^2 \end{aligned} \tag{4-52}$$

where

$$Z = b^{a_1} + b^{a_2} + \ldots + b^{a_N} \tag{4-53}$$

One derives B (second term) in a similar fashion to get

$$B = N Z^{N-1} (1 - b^{\omega_0}) \sum_{r\in G_2} b^{a_r} |(r' | m | r)|^2 \tag{4-54}$$

where

$$(r'|m|r) \equiv {}_i(r'|M_i|r)_i \quad \text{independent of } i \tag{4-55}$$

and use has been made of equation (4-36).

There was no need to solve a combinatorial problem, and result (4-54) agrees with McMillan (1959). All other traces can be done in the same manner, even in higher approximations.

For the special case when (a) $\mathcal{H}_i^{(o)}$ has axial symmetry; (b) the external magnetic field $\underline{H}_o$ is directed along the axis of symmetry (Z-axis); (c) the order of unperturbed energy levels is preserved in the transition to the no-crystalline field case (equation (2-17)); and (d) the relation $[S_i^z, \mathcal{H}_i^{(o)}] = 0$ holds, we may write

$$\hat{M}_+ = \beta g_\perp \sum_i \sum_{\lambda \in G_1} S_{i\lambda+1}^- \tag{4-56}$$

$$\hat{M}_- = \beta g_\perp \sum_i \sum_{\lambda \in G_1} S_{i\lambda}^+ \tag{4-57}$$

$$\overline{\mathcal{H}}_{ij}^{(1)} = \left(\overline{\mathcal{H}}_{ij}^{(1)}\right)_{c.f.} \quad \text{as given by (2-23)}$$

where λ, $S_{i\lambda}^+$, $S_{i\lambda+1}^-$, and G_1 are as defined in Chapter II. A direct comparison between equations (4-56), (4-57) and equations (4-43), (4-44) cannot be made because of the differences in the definitions of G_1 and G_2, and in the labelling procedures. However, it may easily be verified that $\hat{M}_+$, as given by equation (4-56), conforms to the definition (4-27), and that $\hat{M}_-$, as given by equation (4-57), conforms to definition (4-28).

It has been checked, for the specialized problem wherein conditions (a) to (d) (above) hold, that formula (4-15), in the case of an absorption line from the ground state to the first excited state of the unperturbed spin, yields the same final results for the first and second central moments as were obtained by

McMillan and Opechowski (1960); the calculations were done in the first two approximations of McMillan and Opechowski, for the cases of effective spin $S = \frac{1}{2}$ and $S = 1$.

CHAPTER V

The Moment Theorem

1. Relation of Moments to Terms in Hierarchy of Equations.

It is interesting to take note of the identification between the raw moments (moments about the origin) and the first terms on the R.H.S. of the Green's function hierarchy of equations (2-50). The latter may be written

$$E \ll \{A, \bar{\mathcal{H}}\}^p | B \gg_E = \frac{1}{2\pi} \langle [\{A, \bar{\mathcal{H}}\}^p, B] \rangle + \ll \{A, \bar{\mathcal{H}}\}^{p+1} | B \gg_E \qquad (5\text{-}1)$$

$$p = 0,1,2,\ldots$$

Comparing with the expression (4-5) for μ_p, one sees that, apart from a factor $2\pi / \langle [A, B] \rangle$ the identification is complete. It is assumed that conditions (4-3) and (4-4) are fulfilled.

Moreover, if condition (4-14) holds, the hierarchy of equations (5-1) is easily cast into the form

$$(E - \omega_0) \ll \{A, \bar{\mathcal{H}}^{(1)}\}^p | B \gg_E = \frac{1}{2\pi} \langle [\{A, \bar{\mathcal{H}}^{(1)}\}^p, B] \rangle + \ll \{A, \bar{\mathcal{H}}^{(1)}\}^{p+1} | B \gg_E \qquad (5\text{-}2)$$

$$p = 0,1,2,\ldots.$$

It is in this form that the Green's function hierarchy of equations will be used in the remainder of this thesis. Apart from the same factor $2\pi \langle [A,B] \rangle$, one identifies the first terms on the R.H.S. of the latter equations with the central moments, M_p (equation (4-15)).

One may ask whether this identification can be made directly from equation (5-2) and the relation

$$g_{BA}(\omega) = \frac{\lim_{\varepsilon \to 0^+} \mathrm{Im} \ll A | B \gg_{E = \omega - i\varepsilon}}{\lim_{\varepsilon \to 0^+} \int d\omega \, \mathrm{Im} \ll A | B \gg_{E = \omega - i\varepsilon}} \qquad (5\text{-}3)$$

between the Green's function $\ll A|B \gg_E$ and the line shape function $g_{BA}(\omega)$. A proof that this can be done is given in Appendix III.

This identification is, of course, valueless if one wants only to calculate exact moments; the Green's function technique need not be considered at all for this purpose. However, very often the Green's function technique, coupled with a certain decoupling procedure, is used to derive an approximate analytic expression for the line shape function, and it is asked what the associated moments are and how closely they approximate the true moments. The integrations involved are often extremely difficult to carry out. A theorem, closely related to the aforementioned identification, can be proved which provides a relatively simple method for finding the approximate moments, and eliminates the necessity for performing any integrations. Before this theorem is stated and proved, however, an outline of decoupling procedures as they are normally followed, will be given.

2. Decoupling Procedures

First, rewrite (5-2) as follows:

$$e\, G_p = T_p + G_{p+1} \tag{5-2a}$$

where we have replaced $E - \omega_0$ by e (5-4a)

$\ll \{A, \bar{\mathcal{H}}^{(1)}\}^p | B \gg_E$ by G_p (5-4b)

and $\frac{1}{2\pi} \langle [\{A, \bar{\mathcal{H}}^{(1)}\}^p, B] \rangle$ by T_p (5-4c)

A method one might follow would be to write the first q equations as they stand, and in the q+1st to replace G_{q+1} by a linear combination of the q+1 preceding Green's functions, the coefficients (usually thermal averages) being independent of E; i.e.

$$e\,G_0 = T_0 + G_1 \qquad (5\text{-}5a_1)$$

$$e\,G_1 = T_1 + G_2 \qquad (5\text{-}5a_2)$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$e\,G_{q-1} = T_{q-1} + G_q \qquad (5\text{-}5a_q)$$

$$e\,G_q = T_q + \sum_{\ell=0}^{q} d_\ell\, G_\ell \qquad (5\text{-}5a_{q+1})$$

We call this "decoupling at the (q+1)st stage". A closed set of linear equations is obtained which must be solved for G_0, which is simply related to $g_{BA}(\omega)$. (It will be obvious throughout when G_0 stands for the exact G_0 and when it is used to mean the approximate value obtained on solution of the decoupled set of equations.)

This method is found to be unsatisfactory in most cases. Usually G_0 is made up of more elementary Green's functions $G_0^{(\alpha)}$ such that

$$G_0 = \sum_{\alpha=1}^{n} G_0^{(\alpha)} \qquad (5\text{-}6)$$

e.g.

$$G_0 = \ll \sum_i \sum_\lambda A_{i\lambda}^{+} \,|\, \sum_j \sum_{\lambda'} A_{j\lambda'+1}^{-} \gg_E \qquad (5\text{-}7a)$$

and

$$G_0^{(\alpha)} \equiv G_0^{i,\lambda,j,\lambda'} = \ll A_{i\lambda}^{+} \,|\, A_{j\lambda'+1}^{-} \gg_E \qquad (5\text{-}7b)$$

Let us write a separate hierarchy of equations for each of the elementary Green's functions $G_0^{(\alpha)}$:

$$e\,G_0^{(\alpha)} = T_0^{(\alpha)} + G_1^{(\alpha)} \qquad (5\text{-}8a_1)$$

$$e\,G_1^{(\alpha)} = T_1^{(\alpha)} + G_2^{(\alpha)} \qquad (5\text{-}8a_2)$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$e\,G_q^{(\alpha)} = T_q^{(\alpha)} + G_{q+1}^{(\alpha)} \qquad (5\text{-}8a_{q+1})$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

Equations (5-8) represent $\mathcal{N}$ hierarchies of equations, each hierarchy labelled by a different α. They differ from equations (5-2a) in that different A and B have been used in the defining equation (5-2). The $T_r^{(\alpha)}$ are the thermal averages associated with the Green's functions $G_r^{(\alpha)}$. The $G_r^{(\alpha)}$ $(r \neq 0)$ are not meant to be elementary Green's functions, but are defined by equations (5-8), through the given $G_0^{(\alpha)}$ and equations (5-2). (There is no difficulty in picking out which terms are to be grouped with the $T_r^{(\alpha)}$ and which with the $G_r^{(\alpha)}$ in writing equations (5-8); all the $G_r^{(\alpha)}$ vanish in the limit as $e \longrightarrow \infty$, whereas the $T_r^{(\alpha)}$ are independent of e.)

One might want to decouple each hierarchy as follows:

$$G_{q+1}^{(\alpha)} \doteq \sum_{r=0}^{q} h_\alpha^r \, G_r^{(\alpha)} \tag{5-9}$$

where

$$h_\alpha^r \neq h^r \quad \text{independent of} \quad \alpha \tag{5-9a}$$

Each set (labelled by α) of (5-8) is now closed, and can be solved for $G_0^{(\alpha)}$. Then the sum (5-6) can be taken over all the solutions. The above procedure is not equivalent to that leading to equations (5-5), for if we sum equations (5-8) over α, we get the set of equations

$$\begin{aligned} e\, G_0 &= T_0 + G_1 \\ e\, G_1 &= T_1 + G_2 \\ &\vdots \quad\quad \vdots \quad\quad \vdots \\ e\, G_q &= T_q + \sum_{r=0}^{q} \sum_{\alpha} h_\alpha^r \, G_r^{(\alpha)} \end{aligned} \tag{5-10}$$

Because of condition (5-9a), the set (5-10) is not closed, as was the set (5-5).

This method of decoupling is also unsatisfactory in most cases. What usually happens is that $G_1^{(\alpha)}$ is also made up of elementary Green's functions $G_1^{(\alpha)(\beta)}$,

$$G_1^{(\alpha)} = \sum_{\beta} G_1^{(\alpha)(\beta)} \tag{5-11}$$

and one might want to decompose $G_{q+1}^{(\alpha)}$ in terms of the $G_1^{(\alpha)(\beta)}$ with different coefficients for each $(\alpha)(\beta)$ pair. So separate equations for $G_1^{(\alpha)(\beta)}$ are needed. Continuing on in this way, we find that our most general set of equations can be written

$$e\, G_0^{(\alpha)} = T_0^{(\alpha)} + \sum_{\beta} G_1^{(\alpha)(\beta)} \qquad (5\text{-}12a_1)$$

$$e\, G_1^{(\alpha)(\beta)} = T_1^{(\alpha)(\beta)} + \sum_{\gamma} G_2^{(\alpha)(\beta)(\gamma)} \qquad (5\text{-}12a_2)$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$e\, G_q^{(\alpha)(\beta)\ldots(\delta)} = T_q^{(\alpha)(\beta)\ldots(\delta)} + \sum_{\epsilon} {}^{dec}G_{q+1}^{(\alpha)(\beta)\ldots(\delta)(\epsilon)} \qquad (5\text{-}12a_{q+1})$$

where each Green's function that appears is elementary. Here ${}^{dec}G_{q+1}^{(\alpha)(\beta)\ldots(\delta)(\epsilon)}$, the result of some specified decomposition

$$G_{q+1}^{(\alpha)(\beta)\ldots(\delta)(\epsilon)} \longrightarrow {}^{dec}G_{q+1}^{(\alpha)(\beta)\ldots(\delta)(\epsilon)} , \qquad (5\text{-}12b)$$

is some linear combination of all the other elementary Green's functions. Equation (5-12a$_1$) represents n equations, one for each value of α; equation (5-12a$_2$) represents ($n\,m$) equations, where m is the number of β-values; and so on. The number of equations in the set (5-12) is equal to the total number n of elementary Green's functions that appear. We call equation (5-12) our "closed set of decoupled equations".

For convenience, we relabel all the elementary Green's functions in (5-12) by the single subscript α. Equation (5-12) is then rewritten

$$e\, G_\alpha = T_\alpha + \sum_{\beta=1}^{n} C_\alpha^\beta\, G_\beta \qquad \alpha = 1, 2, \ldots, n \qquad (5\text{-}13)$$

where C_α^β are coefficients which may be zero, and are independent of E. The T_α are the thermal averages associated with the G_α, in accordance with equations (2-50).

In order to identify G_0, we call S_0 the set of all values of α such that

$$G_0 = \sum_{\alpha \in S_0} G_\alpha \quad . \tag{5-14}$$

It is then possible to identify $T_0, G_1, T_1, G_2 \ldots T_{q-1}, G_q, T_q$ in terms of the C_α^β and the G_α. For, summing (5-13) over $\alpha \in S_0$, we get

$$e \sum_{\alpha \in S_0} G_\alpha \equiv e\, G_0 = \sum_{\alpha \in S_0} T_\alpha + \sum_{\alpha \in S_0} C_\alpha^{\beta_1} G_{\beta_1} \tag{5-15}$$

where the summation convention (repeated indices are summed over all possible values) has been used, and will be used throughout the rest of the chapter. Comparing with (5-2a) for p=0, we get

$$T_0 = \sum_{\alpha \in S_0} T_\alpha \tag{5-16}$$

$$G_1 = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} G_{\beta_1} \tag{5-17}$$

We also have, still using equations (5-13),

$$e \sum_{\alpha \in S_0} C_\alpha^{\beta_1} G_{\beta_1} \equiv e\, G_1 = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} T_{\beta_1} + \sum_{\alpha \in S_0} C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} G_{\beta_2} \quad . \tag{5-18}$$

Comparison with (5-2a) for p=1 gives

$$T_1 = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} T_{\beta_1} \tag{5-19}$$

$$G_2 = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} G_{\beta_2} \quad . \tag{5-20}$$

In general, for $\ell \leq q$ we can write

$$\overline{T}_\ell = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} \cdots C_{\beta_{\ell-1}}^{\beta_\ell} \overline{T}_{\beta_\ell} \tag{5-21}$$

$$G_\ell = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} \cdots C_{\beta_{\ell-1}}^{\beta_\ell} G_{\beta_\ell} \tag{5-22}$$

as up to this point the decomposition (5-12b), which represents our (q+1)st state decoupling, does not affect the original hierarchy of equations (5-2a). For $\ell > q$, the above identifications ((5-21) and (5-22)) cannot be made. However, defining primed quantities $\overline{T}_\ell'$ and G_ℓ' by

$$\overline{T}_\ell' = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} \cdots C_{\beta_{\ell-1}}^{\beta_\ell} \overline{T}_{\beta_\ell} \tag{5-23}$$

$$G_\ell' = \sum_{\alpha \in S_0} C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} \cdots C_{\beta_{\ell-1}}^{\beta_\ell} G_{\beta_\ell} \tag{5-24}$$

for all ℓ, we can continue equations (5-15) and (5-18) into the infinite set

$$e\, G_\ell' = \overline{T}_\ell' + G_{\ell+1}', \quad \text{all } \ell \tag{5-25}$$

which is based on the closed set of decoupled equations (5-13). Note that

$$\overline{T}_\ell' = \overline{T}_\ell \qquad (\ell \leq q) \tag{5-26a}$$

and

$$G_\ell' = G_\ell \qquad (\ell \leq q) \tag{5-26b}$$

It is of interest to note that one can equivalently define $\overline{T_\ell}'$ and G_ℓ' by equations (5-25), (5-26a), (5-26b), and the decoupled set of equations in which one is interested, e.g. (5-5) or (5-13). Equations (5-23) and (5-24), our previous definitons of $\overline{T_\ell}'$ and G_ℓ' , may then be deduced through the use of equations (5-13), (5-21), and (5-22).

Let us consider, as an example of this alternate definition, the special case of decoupled equations (5-5). Looking at equation ($5\text{-}5a_{q+1}$), we define G_{q+1}' by

$$G_{q+1}' = \sum_{\ell=0}^{q} d_\ell G_\ell \tag{5-27}$$

and write a Green's function equation for it, using equations (5-5) to do so:

$$\begin{aligned} e\, G_{q+1}' &= e \sum_{\ell=0}^{q-1} d_\ell G_\ell + e\, d_q G_q \\ &= \sum_{\ell=0}^{q-1} d_\ell T_\ell + \sum_{\ell=0}^{q-1} d_\ell G_{\ell+1} \\ &\quad + d_q T_q + d_q \sum_{\ell=0}^{q} d_\ell G_\ell \\ &= \sum_{\ell=0}^{q} d_\ell T_\ell + \sum_{\ell=0}^{q} (d_{\ell-1} + d_q d_\ell) G_\ell \end{aligned} \tag{5-28}$$

where in (5-28) we define d_{-1}, d_{-2},... to be identically zero. We then define $\overline{T}_{q+1}'$ by

$$\overline{T}_{q+1}' = \sum_{\ell=0}^{q} d_\ell \overline{T}_\ell \tag{5-29}$$

and G_{q+2}' by

$$G_{q+2}' = \sum_{\ell=0}^{q} (d_{\ell-1} + d_q d_\ell) G_\ell \tag{5-30}$$

We next write an equation for G'_{q+2} to get, in the same way as above,

$$e\,G'_{q+2} = \sum_{\ell=0}^{q} (d_{\ell-1} + d_q d_\ell)\,T_\ell + (\text{Green's functions}) \qquad (5\text{-}31)$$

and define T'_{q+2} by

$$T'_{q+2} = \sum_{\ell=0}^{q} (d_{\ell-1} + d_q d_\ell)\,T_\ell \qquad (5\text{-}32)$$

and so on.

It is this latter definition of the T'_ℓ that is useful in practical applications of the Moment Theorem, which we are now prepared to state.

3. Statement and Proof of Moment Theorem

Theorem: The ℓ^{th} moment M'_ℓ associated with the line shape function derived from the closed set of decoupled equations (5-13) is given by

$$M'_\ell = T'_\ell / T'_0 \qquad (5\text{-}33)$$

for all ℓ.

Corollary I

For (q+1)st-stage decoupling, the first q+1 central moments M_0', M_1', ..., M_q' are exact.

The proof follows immediately from the definition (5-23) of T_ℓ' and the identification (5-21) for $\ell \leq q$.

Corollary II

If one wants a line shape function which gives the first q+1 moments exactly, one cannot afford to decouple before the $(q+1)^{st}$ stage.

The proof is analogous to that for Corollary I, with the additional remark that a thermal average cannot in general be expressed exactly in terms of lower-order thermal averages.

Proof of Theorem

The proof will be given in part for a simple case first, and then in full for the general case.

Case (a): Closed set of equations given by (5-5).

Equations (5-5) form a special case of the set of equations (5-13). For proving this case it is more instructive to use the language of the special case, which means using the definitions of T_ℓ' and G_ℓ' given at the end of Section 2.

Since equations (5-5) represent q+1 linear equations, each G_ℓ $(0 \leq \ell \leq q)$ can be written, by Cramer's Rule, as a quotient of determinants, the denominator being a polynomial one degree higher in e than the numerator. Barring accidental degeneracies, then, each G_ℓ can be written as

$$G_\ell = \sum_{p=1}^{q+1} \frac{A_\ell^p}{e - \varepsilon_p} \qquad (5\text{-}34)$$

which results from the decomposition into partial fractions of the quotient solution. A_ℓ^ρ are certain coefficients independent of E, some of which may be zero. The A_ℓ^ρ are real as is shown in Appendix III for the general case. The $\mathcal{E}_\rho$ are real, distinct, and independent of ℓ . The reality of the $\mathcal{E}_\rho$ follows from the analyticity conditions on the Green's functions. Their independence of ℓ follows from the observation that all the G_ℓ have the same denominators in the quotient of determinants.

Substitution of equation (5-34) into equation (5-5) yields

$$\sum_\rho \frac{(e-\mathcal{E}_\rho+\mathcal{E}_\rho)A_\ell^\rho}{e-\mathcal{E}_\rho} = T_\ell + \sum_\rho \frac{A_{\ell+1}^\rho}{e-\mathcal{E}_\rho}, \quad 0 \le \ell < g \tag{5-35}$$

$$\sum_\rho \frac{(e-\mathcal{E}_\rho+\mathcal{E}_\rho)A_g^\rho}{e-\mathcal{E}_\rho} = T_g + \sum_{\ell=0}^{g} d_\ell \sum_\rho \frac{A_\ell^\rho}{e-\mathcal{E}_\rho} \,. \tag{5-36}$$

Equating coefficients of $(e-\mathcal{E}_\rho)^{-1}$ results in three conditional equations:

$$\sum_\rho A_\ell^\rho = T_\ell \,, \quad 0 \le \ell \le g \tag{5-37}$$

$$\mathcal{E}_\rho A_\ell^\rho = A_{\ell+1}^\rho \,, \quad 0 \le \ell < g \tag{5-38}$$

$$\mathcal{E}_\rho A_g^\rho = \sum_{\ell=0}^{g} d_\ell A_\ell^\rho \tag{5-39}$$

Now, using equations (5-3), (5-34), (5-4a) and the asymptotic formula

$$\lim_{\varepsilon \to 0^+} \frac{1}{x \pm i\varepsilon} = P\left(\frac{1}{x}\right) \mp i\pi\delta(x) \tag{5-40}$$

where P denotes the Cauchy principal value, we find

$$M_r' = \int d\omega\ (\omega-\omega_0)^r g_{BA}(\omega)$$

$$= \frac{\lim_{\varepsilon\to 0^+} \int d\omega\ (\omega-\omega_0)^r \operatorname{Im} G_0|_{E=\omega-i\varepsilon}}{\lim_{\varepsilon\to 0^+} \int d\omega\ \operatorname{Im} G_0|_{E=\omega-i\varepsilon}}$$

$$= \frac{\lim_{\varepsilon\to 0^+} \int d\omega\ (\omega-\omega_0)^r \operatorname{Im} \sum_\rho \frac{A_0^\rho}{E-\omega_0-\varepsilon_\rho}\Big|_{E=\omega-i\varepsilon}}{\lim_{\varepsilon\to 0^+} \int d\omega\ \operatorname{Im} \sum_\rho \frac{A_0^\rho}{E-\omega_0-\varepsilon_\rho}\Big|_{E=\omega-i\varepsilon}}$$

$$= \frac{\int d\omega\ (\omega-\omega_0)^r \sum_\rho A_0^\rho\ \delta(\omega-\omega_0-\varepsilon_\rho)}{\int d\omega \sum_\rho A_0^\rho\ \delta(\omega-\omega_0-\varepsilon_\rho)}$$

$$= \frac{\sum_\rho A_0^\rho (\varepsilon_\rho)^r}{\sum_\rho A_0^\rho} \quad , \tag{5-41}$$

From (5-38) and (5-39), if $0 \le r \le q$,

$$(\varepsilon_\rho)^r A_0^\rho = \varepsilon_\rho^{r-1} A_1^\rho = \cdots = \varepsilon_\rho A_{r-1}^\rho = A_r^\rho \tag{5-42}$$

and

$$\sum_\rho A_0^\rho (\varepsilon_\rho)^r = \sum_\rho A_r^\rho = T_r \quad \text{from (5-37)}$$

$$= T_r' \quad \text{from (5-26a)} . \tag{5-43}$$

So, for $r \leq q$, equation (5-41) yields

$$M_r' = \overline{T}_r' / \overline{T}_0' \quad . \tag{5-44}$$

If $r = q+1$, we have

$$\begin{aligned} \sum_p (\varepsilon_p)^{q+1} A_0^p &= \sum_p \varepsilon_p A_q^p && \text{from (5-38)} \\ &= \sum_p \sum_{\ell=0}^{q} d_\ell A_\ell^p && \text{from (5-39)} \\ &= \sum_{\ell=0}^{q} d_\ell \overline{T}_\ell && \text{from (5-37)} \\ &= \overline{T}_{q+1}' && \text{from (5-29)} \end{aligned} \tag{5-45}$$

and so

$$M_{q+1}' = \overline{T}_{q+1}' / \overline{T}_0' \tag{5-46}$$

from (5-41), (5-44), and (5-45). The theorem is thus verified for $\ell = 0,1\ldots,$ q+1 (equation (5-33)). The proof is not continued for higher values of r for this special case, as the notation becomes quite unwieldy.

Case (b): General closed set of equations (5-13).

For this case we make use of the definitions (5-23) and (5-24) of $\overline{T}_\ell'$ and G_ℓ'.

From the theory of linear equations, the solution of equation (5-13) is given as a quotient of determinants, the denominator being a polynomial one degree higher in e than the numerator. Barring accidental degeneracies then, each G_α can be written as

$$G_\alpha = \sum_{p=1}^{n} \frac{A_\alpha^p}{e - \varepsilon_p} \tag{5-47}$$

which results from the decomposition into partial fractions of the quotient solution. n, the number of elementary Green's functions, is the degree of the polynomial comprising the denominator; A_α^ρ are certain coefficients independent of E, some of which may be zero, and the ε_ρ are real, distinct, and independent of α. The reality of the ε_ρ follows from the condition that the Green's functions be analytic on the upper and lower half-planes. Their independence of α follows from the observation that all the G_α have the same denominators in the above-mentioned quotient of determinants.

Substitution of (5-47) into (5-13) yields

$$\sum_\rho \frac{(e-\varepsilon_\rho+\varepsilon_\rho)A_\alpha^\rho}{e-\varepsilon_\rho} = T_\alpha + \sum_\rho \frac{C_\alpha^{\beta_1} A_{\beta_1}^\rho}{e-\varepsilon_\rho} \qquad (5\text{-}48)$$

where the summation convention is still in use. Equating coefficients of $(e-\varepsilon_\rho)^{-1}$ results in two conditional equations:

$$\sum_\rho A_\alpha^\rho = T_\alpha \qquad \text{all } \alpha \qquad (5\text{-}49)$$

$$\varepsilon_\rho A_\alpha^\rho = C_\alpha^{\beta_1} A_{\beta_1}^\rho \qquad \text{all } \alpha \qquad (5\text{-}50)$$

It is important for the proof that the A_α^ρ be shown to be real. This is done in Appendix IV.

Multiplying equation (5-50) by 1, ε_ρ, $(\varepsilon_\rho)^2$,... successively, and using (5-49), one finds

$$\sum_\rho \varepsilon_\rho A_\alpha^\rho = \sum_\rho C_\alpha^{\beta_1} A_{\beta_1}^\rho = C_\alpha^{\beta_1} \sum_\rho A_{\beta_1}^\rho = C_\alpha^{\beta_1} T_{\beta_1}$$

$$\sum_\rho (\varepsilon_\rho)^2 A_\alpha^\rho = \sum_\rho \varepsilon_\rho C_\alpha^{\beta_1} A_{\beta_1}^\rho = C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} T_{\beta_2}$$

$$\vdots$$

$$\sum_\rho (\varepsilon_\rho)^\ell A_\alpha^\rho = C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2} \cdots C_{\beta_{\ell-1}}^{\beta_\ell} T_{\beta_\ell} \qquad (5\text{-}51)$$

From equations (5-3), (5-4a), (5-4b) for p=0, (5-47), (5-40), (5-14), and the reality of the A_α^ρ, the moments of $g_{BA}(\omega)$ are given by

$$M_\ell' = \frac{\lim_{\varepsilon\to 0^+}\int d\omega\,(\omega-\omega_0)^\ell\,\mathrm{Im}\,G_0|_{E=\omega-i\varepsilon}}{\lim_{\varepsilon\to 0^+}\int d\omega\,\mathrm{Im}\,G_0|_{E=\omega-i\varepsilon}}$$

$$= \frac{\lim_{\varepsilon\to 0^+}\int d\omega\,(\omega-\omega_0)^\ell\,\mathrm{Im}\sum_{\alpha\in S_0} G_\alpha|_{E=\omega-i\varepsilon}}{\lim_{\varepsilon\to 0^+}\int d\omega\,\mathrm{Im}\sum_{\alpha\in S_0} G_\alpha|_{E=\omega-i\varepsilon}}$$

$$= \frac{\lim_{\varepsilon\to 0^+}\int d\omega\,(\omega-\omega_0)^\ell\sum_{\alpha\in S_0}\sum_\rho \mathrm{Im}\left(A_\alpha^\rho/E-\omega_0-\varepsilon_\rho\right)|_{E=\omega-i\varepsilon}}{\lim_{\varepsilon\to 0^+}\int d\omega\sum_{\alpha\in S_0}\sum_\rho \mathrm{Im}\left(A_\alpha^\rho/E-\omega_0-\varepsilon_\rho\right)|_{E=\omega-i\varepsilon}}$$

$$= \frac{\int d\omega\,(\omega-\omega_0)^\ell\sum_{\alpha\in S_0}\sum_\rho A_\alpha^\rho\,\delta(\omega-\omega_0-\varepsilon_\rho)}{\int d\omega\sum_{\alpha\in S_0}\sum_\rho A_\alpha^\rho\,\delta(\omega-\omega_0-\varepsilon_\rho)}$$

$$= \frac{\sum_{\alpha\in S_0}\sum_\rho (\varepsilon_\rho)^\ell A_\alpha^\rho}{\sum_{\alpha\in S_0}\sum_\rho A_\alpha^\rho}$$

$$= \sum_{\alpha\in S_0} C_\alpha^{\beta_1} C_{\beta_1}^{\beta_2}\cdots C_{\beta_{\ell-1}}^{\beta_\ell}\,T_{\beta_\ell}\Big/\sum_{\alpha\in S_0} T_\alpha \qquad \text{by (5-51)}$$

$$= T_\ell'/T_0' \qquad \text{by definition (5-29)}$$

This completes our proof.

4. Summary on Use of Theorem.

It may be worthwhile here to summarize this chapter indicating how the theorem would be used. Examples of its use will be given in the following chapter.

The line shape function can be expressed in terms of a Green's function G_0 and the equation for G_0 leads to a hierarchy of equations involving higher-order Green's functions G_ℓ . This hierarchy is decoupled in some manner leading to a closed set of equations which can be solved for the approximate G_0 . One could then find the moments of the line shape by suitable integrations with the approximate line shape function. The theorem shows that this integration is not necessary. The approximate moments up to the stage q+1 at which the decoupling was done are just the usual thermal averages appearing in the equations and agree with the exact moments. To find the higher moments of the approximate line shape one continues the closed hierarchy of equations. In this continuation no new Green's functions appear; each time a G_{q+1} Green's function appears in an equation it is decomposed with the rule first used. The thermal averages appearing in these higher equations are the appropriate higher moments of the approximate line shape function.

This procedure for finding moments has the advantage that it does not require one to solve equation (5-13) explicitly; one need specify only the decomposition (5-12b) that is being used.

CHAPTER VI

Resonance Line Shape Problem

1. Decoupling Methods

At the beginning of Chapter IV, the properties demanded of a suitable decoupling technique are outlined. These are the tractability, degree of complexity, and faithfulness of the resulting closed set of linear equations. It is, in any specific case, a simple matter to determine whether a set of equations is complex or tractable. It is the question of faithfulness that will be dealt with in this chapter.

We postulate a faithfulness criterion: one decoupling procedure is said to be more faithful than another if the first few moments of its consequent line shape are closer to the true moments in some valid approximation.

The phrase "in some valid approximation" is inserted, as expressions for the moments are invariably given in terms of thermal averages; and even the thermal average of S_i^z has never been given exactly.

The criterion is practical, for the moment theorem of the last chapter immediately enables one to write down expressions for the moments which are to be compared with the true moments. In line with this practical approach, only the first few moments are usually asked for, as higher moments become increasingly difficult to calculate in any approximation.

Our criterion will now be used to investigate the relative faithfulness of two specific decoupling methods, when these are applied to the problem of finding the paramagnetic resonance line shape function associated with the physical system described by the no-crystalline field Hamiltonian (2-9), where $\mathcal{H}_j^{(0)}$ and $\overline{\mathcal{H}}_{ij}^{(1)}$ are given by equations (2-11) and (2-12a) respectively. One method we shall call the excess-over-random (EOR) method; the other, due to Tomita and Tanaka (1963), which is a partial excess-over-random method, we shall refer to as the T-T method.

We specialize our physical system still further by requiring that it consist of spins having S = ½. For this case, from

$$S^2 = (S_i^z)^2 = \frac{1}{4} \quad , \quad (S = 1/2) \tag{6-1}$$

and the well-known commutation relations for spin operators, the following relations can be proved:

$$\begin{aligned} S_i^- S_i^z &= -S_i^z S_i^- = +\tfrac{1}{2} S_i^- \\ S_i^+ S_i^z &= -S_i^z S_i^+ = -\tfrac{1}{2} S_i^+ \\ S_i^- S_i^+ - \tfrac{1}{2} &= \tfrac{1}{2} - S_i^+ S_i^- = -S_i^z \\ S_i^+ S_i^+ &= S_i^- S_i^- = 0 \end{aligned} \tag{6-2}$$

The significance of the above relations is that any product of two spin operators at one lattice site can be reduced to a linear combination of single spin operators.

The EOR method, which takes full advantage of relations (6-2), proceeds as follows: One rewrites the Green's function equations (2-50) for the "ordinary" Green's functions $[A| \equiv [A/B] \equiv \ll A/B \gg_E$ in terms of comulant Green's functions (A/ = (A/B) which are defined by

$$[1| = (1| \tag{6-3a}$$

$$[12| = \langle 1\rangle (2| + \langle 2\rangle (1| + (12| \tag{6-3b}$$

$$\begin{aligned} [123| = {} & \langle 1\rangle (23| + \langle 2\rangle (13| + \langle 3\rangle (12| \\ & + \langle 23\rangle (1| + \langle 13\rangle (2| + \langle 12\rangle (3| + (123| \end{aligned} \tag{6-3c}$$

etc., where the numerals "1", "2",... represent various operators. After

the above decompositions, one stops at a certain order and discards the highest-order cumulant Green's function. For example, in second-stage decoupling, one stops after equation (6-3c) and neglects the cumulant Green's function $(123|$, supposing it to be small. One of course verifies that the operators "1" and "2" in, for instance, $[123|$, are associated with different lattice sites. Otherwise, the product of operators "1" and "2" is to be treated as a single operator "12" in the above decompositions. As an example, the Green's function $[S_i^z S_i^z S_j^z|$ $(i \neq j)$ for the case S = ½, must be changed to $\frac{1}{4}[S_j^z|$ before any decompositions are made.

The T-T method proceeds in the same manner, with the one essential difference that products of operators associated with the same lattice site are not treated as a single product operator in the decompositions (6-3).

The first two Green's function equations, written for the elementary Green's functions, are

$$e\langle\langle S_i^+|S_e^-\rangle\rangle_E = \frac{1}{2\pi}\langle[S_i^+, S_e^-]\rangle + \sum_j A_{ij}\langle\langle S_i^z S_j^+|S_e^-\rangle\rangle_E - \sum_j C_{ij}\langle\langle S_j^z S_i^+|S_e^-\rangle\rangle_E \tag{6-4a}$$

$$e\langle\langle S_p^z S_i^+|S_e^-\rangle\rangle_E = \frac{1}{2\pi}\langle[S_p^z S_i^+, S_e^-]\rangle + \sum_j A_{ij}\langle\langle S_p^z S_i^z S_j^+|S_e^-\rangle\rangle_E - \sum_j C_{ij}\langle\langle S_p^z S_i^+ S_j^z|S_e^-\rangle\rangle_E - \frac{1}{2}\sum_j A_{pj}\langle\langle S_p^- S_j^+ S_i^+|S_e^-\rangle\rangle_E + \frac{1}{2}\sum_j A_{pj}\langle\langle S_j^- S_p^+ S_i^+|S_e^-\rangle\rangle_E . \tag{6-4b}$$

Note that we in fact want to find

$$G_0 = \sum_i \sum_e \langle\langle S_i^+|S_e^-\rangle\rangle_E . \tag{6-5}$$

These equations hold for any effective spin S.

Second-stage decoupling by the EOR method, for the case S=1/2, consists in making the following replacements:

$$\ll S_\rho^z S_i^z S_j^+ | S_\ell^- \gg_E \xrightarrow[\rho \neq i \neq j]{} \mu \ll S_i^z S_j^+ | S_\ell^- \gg_E + \mu \ll S_\rho^z S_j^+ | S_\ell^- \gg_E + \left(\langle S_\rho^z S_i^z \rangle - 2\mu^2 \right) \ll S_j^+ | S_\ell^- \gg_E \tag{6-6a}$$

$$\ll S_\rho^- S_j^+ S_i^+ | S_\ell^- \gg_E \xrightarrow[\rho \neq i \neq j]{} \langle S_\rho^- S_j^+ \rangle \ll S_i^+ | S_\ell^- \gg_E + \langle S_\rho^- S_i^+ \rangle \ll S_j^+ | S_\ell^- \gg_E \tag{6-6b}$$

where $\mu \equiv \langle S_i^z \rangle$ is independent of i by translational invariance. When any two of p,i, and j are equal, use of equations (6-2) ensures that no new Green's functions are present, and hence that the resulting set of decoupled equations is closed.

Second-stage decoupling by the T-T method consists in making the replacements

$$\ll S_\rho^z S_i^z S_j^+ | S_\ell^- \gg_E \longrightarrow \mu \ll S_i^z S_j^+ | S_\ell^- \gg_E + \mu \ll S_\rho^z S_j^+ | S_\ell^- \gg_E + \left(\langle S_\rho^z S_i^z \rangle - 2\mu^2 \right) \ll S_j^+ | S_\ell^- \gg_E \tag{6-7a}$$

$$\ll S_\rho^- S_j^+ S_i^+ | S_\ell^- \gg_E \longrightarrow \langle S_\rho^- S_j^+ \rangle \ll S_i^+ | S_\ell^- \gg_E + \langle S_\rho^- S_i^+ \rangle \ll S_j^+ | S_\ell^- \gg_E \tag{6-7b}$$

for all p,j, and i.

It may be seen that in the EOR method certain correlations, namely auto-correlations, are retained in their exact form, while in the T-T method they are approximated. Thus, if we take p = i≠j in equation (6-7a), the replacement

$$\frac{1}{4} \ll S_j^+ | S_\ell^- \gg_E \longrightarrow 2\mu \ll S_i^z S_j^+ | S_\ell^- \gg_E + \left(\frac{1}{4} - 2\mu^2 \right) \ll S_j^+ | S_\ell^- \gg_E \tag{6-7c}$$

is effectively performed in the T-T method; in the EOR method, the left-hand side of (6-7c) is retained without approximation.

Substituting equations (6-6) and (6-7) into equation (6-4), the EOR-decoupled equations are

$$e\left[{}^{+}_{i}\right| = \frac{1}{2\pi}\delta_{i\ell}\cdot 2\mu + \sum_j A_{ij}\left[{}^{z}_{i}{}^{+}_{j}\right| - \sum_j C_{ij}\left[{}^{z}_{j}{}^{+}_{i}\right| \tag{6-8a}$$

and

$$\begin{aligned} e\left[{}^{z}_{p}{}^{+}_{i}\right| = {} & \frac{1}{2\pi}\left(2\delta_{i\ell}\langle S_p^z S_i^z\rangle - \delta_{p\ell}\langle S_p^- S_i^+\rangle\right) + \frac{1}{4}\sum_j A_{ij}\delta_{ip}\left[{}^{+}_{j}\right| \\ & - \frac{1}{2}\sum_j C_{ij}\delta_{ip}\left[{}^{z}_{j}{}^{+}_{i}\right| - \frac{1}{4}C_{ip}\left[{}^{+}_{i}\right| + \frac{1}{4}A_{ip}\left[{}^{+}_{p}\right| \\ & - \frac{1}{4}\sum_j A_{ij}\delta_{ip}\left[{}^{+}_{j}\right| + \frac{1}{2}\sum_j A_{ij}\delta_{ip}\left[{}^{z}_{i}{}^{+}_{j}\right| \\ & + \sum_j A_{ij}(1-\delta_{ip}-\delta_{jp})\left\{\mu\left[{}^{z}_{p}{}^{+}_{j}\right| + \mu\left[{}^{z}_{i}{}^{+}_{j}\right| + \left(\langle S_p^z S_i^z\rangle - 2\mu^2\right)\left[{}^{+}_{j}\right|\right\} \\ & - \sum_j C_{ij}(1-\delta_{ip}-\delta_{jp})\left\{\mu\left[{}^{z}_{j}{}^{+}_{i}\right| + \mu\left[{}^{z}_{p}{}^{+}_{i}\right| + \left(\langle S_j^z S_p^z\rangle - 2\mu^2\right)\left[{}^{+}_{i}\right|\right\} \\ & - \frac{1}{2}\sum_j A_{pj}(1-\delta_{ij}-\delta_{ip})\left\{\langle S_p^- S_j^+\rangle\left[{}^{+}_{i}\right| + \langle S_p^- S_i^+\rangle\left[{}^{+}_{j}\right|\right. \\ & \left. - \langle S_j^- S_p^+\rangle\left[{}^{+}_{i}\right| - \langle S_j^- S_i^+\rangle\left[{}^{+}_{p}\right|\right\} \end{aligned} \tag{6-8b}$$

where we have used the notation

$$\begin{aligned} \left[{}^{+}_{i}\right| &\equiv \ll S_i^+ | S_e^- \gg_E \\ \left[{}^{z}_{j}{}^{+}_{i}\right| &\equiv \ll S_j^z S_i^+ | S_e^- \gg_E \end{aligned} \tag{6-9}$$

and the T-T decoupled equations are

$$e\left[{}^{+}_{i}\right| = \frac{1}{2\pi}\,\delta_{il}\cdot 2\mu + \sum_j A_{ij}\left[{}^{z}_{i}{}^{+}_{j}\right| - \sum_j C_{ij}\left[{}^{z}_{j}{}^{+}_{i}\right| \qquad (6\text{-}10a)$$

and

$$\begin{aligned} e\left[{}^{z}_{p}{}^{+}_{i}\right| = {} & \frac{1}{2\pi}\left(2\delta_{il}\langle S_p^z S_i^z\rangle - \delta_{pl}\langle S_p^- S_i^+\rangle\right) \\ & + \sum_j A_{ij}\left\{\mu\left[{}^{z}_{p}{}^{+}_{j}\right| + \mu\left[{}^{z}_{i}{}^{+}_{j}\right| + \left(\langle S_p^z S_i^z\rangle - 2\mu^2\right)\left[{}^{+}_{j}\right|\right\} \\ & - \sum_j C_{ij}\left\{\mu\left[{}^{z}_{j}{}^{+}_{i}\right| + \mu\left[{}^{z}_{p}{}^{+}_{i}\right| + \left(\langle S_j^z S_p^z\rangle - 2\mu^2\right)\left[{}^{+}_{i}\right|\right\} \\ & - \frac{1}{2}\sum_j A_{pj}\left\{\langle S_p^- S_j^+\rangle\left[{}^{+}_{i}\right| + \langle S_p^- S_i^+\rangle\left[{}^{+}_{j}\right| \right. \\ & \left. - \langle S_j^- S_p^+\rangle\left[{}^{+}_{i}\right| - \langle S_j^- S_i^+\rangle\left[{}^{+}_{p}\right|\right\} \end{aligned} \qquad (6\text{-}10b)$$

Other types of second-stage decoupling may certainly be tried. One type that seems worthy of consideration is due to Callen (1963). It makes use of the fact that S_i^z may be expressed in two ways in terms of $S_i^- S_i^+$ and $S_i^+ S_i^-$ for S = ½, i.e.

$$S_i^z = \tfrac{1}{2}\left(S_i^+ S_i^- - S_i^- S_i^+\right) \qquad (6\text{-}11a)$$

and

$$S_i^z = \tfrac{1}{2} - S_i^- S_i^+ \,. \qquad (6\text{-}11b)$$

S_i^z is replaced by

$$S_i^z = \tfrac{1}{2}\alpha\left(S_i^+ S_i^- - S_i^- S_i^+\right) + (1-\alpha)\left(\tfrac{1}{2} - S_i^- S_i^+\right) \qquad (6\text{-}11c)$$

after which decoupling proceeds by the usual EOR method. Here α is an arbitrary parameter which must be fixed by some suitable physical criterion. The Callen method will not be considered in this thesis, as the calculations become very long and involved.

Other possible methods have been looked at and tested on the Ising model Hamiltonian, but they were found to be of far less value than the methods being considered here.

From Corollary I to the Moment Theorem, the first moment, derived from both the EOR- and the T-T-decoupled equations (6-8) and (6-10), is exact, since q = 1. Let us look,then, at the second moment. By use of the procedure suggested by the Moment Theorem, one arrives at the following expressions for M_2(T-T) and M_2(EOR) :

$$M_2(T\text{-}T) = -\frac{1}{2\pi}\cdot\frac{1}{T_0}\sum_{i\ell_j} B_{i\ell}\Big\{-2\mu B_{ij}\left(\langle S_i^z S_j^z\rangle + \langle S_\ell^z S_j^z\rangle + \langle S_\ell^z S_i^z\rangle\right) - \mu A_{ij}\left(\langle S_i^- S_j^+\rangle + \langle S_\ell^- S_j^+\rangle\right) - \mu A_{\ell j}\left(\langle S_\ell^- S_j^+\rangle + \langle S_\ell^- S_i^+\rangle - \langle S_j^- S_\ell^+\rangle - \langle S_j^- S_i^+\rangle\right) + \mu C_{ij}\left(\langle S_\ell^- S_i^+\rangle + \langle S_j^- S_i^+\rangle\right) + 4\mu^2 B_{ij}\Big\} \tag{6-12}$$

$$M_2(EOR) = M_2(T\text{-}T) + \frac{2\mu}{2\pi T_0}\sum_{i\ell}(B_{i\ell})^2\Big\{\langle S_\ell^- S_i^+\rangle + 2\left(\mu^2 - \langle S_i^z S_\ell^z\rangle\right)\Big\} \quad ; \left[T_0 = \mu N/\pi\right]. \tag{6-13}$$

The correct expression for M_2, denoted here by M_2(CORRECT), is derived from equation (4-15) with

$$A = \sum_i S_i^+ \tag{6-14a}$$

$$B = \sum_j S_j^- \tag{6-14b}$$

It is given by

$$M_2(\text{CORRECT}) = -\frac{1}{2\pi T_0}\sum_{ij\ell} B_{i\ell}\{A_{ij}(2\langle S_\ell^z S_i^z S_j^z\rangle - \langle S_\ell^z S_i^- S_j^+\rangle - \langle S_\ell^- S_i^z S_j^+\rangle) - C_{ij}(2\langle S_\ell^z S_j^z S_i^z\rangle - \langle S_\ell^z S_j^- S_i^+\rangle - \langle S_\ell^- S_j^z S_i^+\rangle) - A_{\ell j}(\langle S_\ell^- S_j^+ S_i^z\rangle + \langle S_\ell^- S_j^z S_i^+\rangle - \langle S_j^- S_\ell^+ S_i^z\rangle - \langle S_j^- S_\ell^z S_i^+\rangle)\} \qquad (6\text{-}15)$$

To compare these formulae for the second central moment, we use the McMillan and Opechowski approximation technique which was described in Chapter IV in the section after equation (4-35). The following relations, valid to $(MO)_2$ and for $S = \frac{1}{2}$, are needed for our proposed comparison.

$$\mu = \mu_0 + \beta\bar{C}\mu_0(\mu_0^2 - 1/4) \quad , \quad (\beta = 1/k_B T)$$

$$\langle S_i^z S_\ell^z\rangle - \mu^2 = -\beta C_{i\ell}(\mu_0^2 - 1/4)^2$$

$$\langle S_\ell^- S_i^+\rangle = \beta/2\, A_{i\ell}(\mu_0^2 - 1/4)$$

$$\langle S_p^z S_q^z S_r^z\rangle = \mu_0^3 + \beta\mu_0(\mu_0^2 - 1/4)\left[(3\bar{C} - \Sigma)\mu_0^2 + 1/4\,\Sigma\right] \qquad (6\text{-}16)$$

$$\langle S_r^z S_p^- S_q^+\rangle = \frac{\beta\mu_0}{2} A_{pq}(\mu_0^2 - 1/4)$$

where

$$\mu_0 = Tr\left[e^{-\beta\mathcal{H}^{(0)}} S_i^z\right] / Tr\, e^{-\beta\mathcal{H}^{(0)}}$$

is the first-approximation part of μ, and is independent of i,

$$\overline{C} = \sum_{\ell} C_{i\ell}$$

is independent of i by translational invariance,

and $$\Sigma = C_{pq} + C_{qr} + C_{pr} \quad .$$

Substituting the above expressions into (6-12), (6-13), and (6-15) the expressions for M_2 become, in $(MO)_1$,

$$M_2(T\text{-}\bar{T}) = M_2(EOR) = M_2(CORRECT)$$
$$= \frac{1}{2\pi T_0}\left\{2\mu_0^3 \sum_{ij\ell} B_{i\ell} B_{j\ell} + 2\mu_0\left(\tfrac{1}{4} - \mu_0^2\right)\sum_{i\ell} (B_{i\ell})^2\right\}; \quad (6\text{-}17)$$

in $(MO)_2$

$$M_2(T\text{-}\bar{T}) = \text{R.H.S. of (6-17)} - \frac{1}{2\pi T_0}\beta\mu_0\left(\mu_0^2 - 1/4\right)\sum_{i\ell j} B_{i\ell} B_{ij}\left\{2\left(\mu_0^2 - 4\right)(C_{i\ell} + C_{ij} + C_{j\ell}) + \tfrac{1}{2}(A_{i\ell} + A_{ij}) - 6\mu_0^2\overline{C}\right\} \quad (6\text{-}18)$$

and

$$M_2(EOR) = M_2(CORRECT) = \text{R.H.S. of (6-18)} + \frac{2\mu_0\beta}{2\pi T_0}\left(\mu_0^2 - 1/4\right) \times$$
$$\times \sum_{i\ell} (B_{i\ell})^2\left\{\tfrac{1}{2}A_{i\ell} + 2C_{i\ell}\left(\mu_0^2 - 1/4\right)\right\}. \quad (6\text{-}19)$$

And so the second-approximation part of $M_2(T\text{-}\bar{T})$ is found to be in error. Moreover, this error is not O(1/N) of the correct second-approximation part. This may be seen by comparing, for example, the terms

$$\sum_{i\ell} (B_{i\ell})^2 C_{i\ell}$$

and

$$\sum_{i\ell j} B_{i\ell} B_{ij} C_{i\ell} \quad .$$

The first term is not O(1/N) of the second even though the latter involves an extra summation. This is so because B_{il} and C_{il} fall off as rapidly as $1/|\underline{r}_i - \underline{r}_l|^3$ with increasing distance between lattice sites. O'Reilly and Tsang (1962) have done summations like the above for the special case of Calcium Fluoride crystals, bearing out this statement. Note, however, the error is nil when T = 0, as in this limit

$$\mu_0^2 - 1/4 = 0$$

and also when $T = \infty$, as then

$$\mu_0 = 0$$

We now look at third central moments. With considerable work it can be shown that, to $(MO)_1$,

$$M_3(EOR) = M_3(CORRECT)$$
$$= \frac{N}{2\pi T_0}\left\{-2\mu_0^4(\overline{B})^3 - 2\mu_0^2(\mu_0^2-1/4)\left[\overline{ABB} + 2\,\overline{BBB} - 3\,\overline{B}\;\overline{BB} - \overline{A}\;\overline{BB} + \frac{1}{N}\sum_{ij} B_{ij}A_{ji}B_{ij}\right]\right\} \qquad (6\text{-}20)$$

where the notation

$$\overline{ABCD\ldots} = \sum_i A_{il}B_{il}C_{il}D_{il}\ldots$$

has been used.

$M_3(T\text{-}T)$ is more difficult to compute, even to $(MO)_1$, but it can be shown to be in error generally by showing it to be so for the Ising model. For this case

$$M_3(CORRECT) = \frac{N}{2\pi T_0}\,4\mu_0^2\epsilon^3 \quad ; \quad [T_0 = \mu N/\pi] \qquad (6\text{-}21)$$

and

$$M_3(T\text{-}T) = M_3(CORRECT) - \frac{8\epsilon^3 N}{2\pi T_0}\mu_0^2(\mu_0^2 - 1/4) \qquad (6\text{-}22)$$

Again it is seen that the error is not of O(1/N), and that it vanishes only in the limits T=0 and T = ∞.

The following table is drawn up in order to highlight the differences in moments calculated by the EOR and T-T methods. The ticks represent areas of agreement with the correct values, the crosses, disagreement.

	M_1			M_2		M_3	
	$(MO)_1$	$(MO)_2$	$(MO)_3$	$(MO)_1$	$(MO)_2$	$(MO)_1$	$(MO)_2$
T-T	✓	✓	✓	✓	×	×	×
EOR	✓	✓	✓	✓	✓	✓	×

By our criterion, it follows that EOR second-stage decoupling should yield a more faithful line shape function than the method of Tomita and Tanaka.

2. Solution of Equations.

When one comes to consider the solution of the EOR and T-T-decoupled equations (6-8) and (6-10), the tractability requirement assumes extreme importance. The T-T equations turn out to be completely admissible of an analytic solution in Fourier-transformed space, while the EOR equations, which are almost identical, have some added terms which increase the number of simultaneous equations which must be solved for G_{1_0} to something of the order of N.

Moreover, the T-T method yields a set of tractable equations for spin values higher than ½, and can easily be extended to third-stage decoupling. The EOR method, on the other hand, becomes prohibitively complicated when higher spin values and higher-stage decoupling are used.

For the reason that T-T second-stage decoupling does not conform sufficiently to the complexity requirement at high temperatures(i.e., temperatures in the paramagnetic range), Tomita and Tanaka extended their calculations to include third-stage decoupling. Now, T-T third-stage decoupling leads to equations which, according to our criterion, are even more faithful than EOR second-stage decoupling. This follows from Corollary I to the moment theorem, which tells us that the M_2, as well as the M_1, resulting from a third-stage decoupling, is exact. For the above reasons, no serious attempt will be made to solve the second-stage EOR-decoupled equations other than formally. A simple case will be considered, however, to show that these equations satisfy the complexity requirement, even at high temperatures.

The first two Fourier-transformed second-stage T-T-decoupled equations, derived from the spatial equations (6-10) are

$$\{E - \Delta_0(k)\}\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| = g_k^+ + \frac{1}{N}\sum_q D(q,k-q)\left(\begin{smallmatrix}0 & +\\k-q & q\end{smallmatrix}\right| \tag{6-23a}$$

and

$$\{E - \Delta_0(q)\}\left(\begin{smallmatrix}0 & +\\k-q & q\end{smallmatrix}\right| = g^{0\,+}_{k-q\;\;q} + \frac{1}{N} R(k,q)\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| \tag{6-23b}$$

where $$\Delta_0(q) = w_0 + \frac{\langle 0\rangle}{N} D(q,0) = w_0 + \mu D(q,0) \tag{6-24a}$$

$$R(k,q) = D(k,q-k)\,\gamma^0_{k-q\;\;q-k} + C(q,k)\,\gamma^{-\;+}_{-q\;\;q} \tag{6-24b}$$

$$D(q,q') = A(q) - C(q') \tag{6-24c}$$

$$C(q,q') = \frac{1}{2}\left(A(q) - A(q')\right) \tag{6-24d}$$

$$A(k) = \frac{1}{N}\sum_i \sum_j e^{ik\cdot(i-j)} A_{ij} \tag{6-24e}$$

and the notation of Tomita and Tanaka

$$\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| \equiv \left(\begin{smallmatrix}+\\k\end{smallmatrix}\middle|\begin{smallmatrix}-\\-k\end{smallmatrix}\right) \equiv \left[\begin{smallmatrix}+\\k\end{smallmatrix}\middle|\begin{smallmatrix}-\\-k\end{smallmatrix}\right]$$

$$= \sum_{\ell}\sum_{j} e^{ik\cdot(j-\ell)}\left[\begin{smallmatrix}+\\j\end{smallmatrix}\middle|\begin{smallmatrix}-\\\ell\end{smallmatrix}\right] = \sum_{\ell}\sum_{j} e^{ik\cdot(j-\ell)} \ll S_j^+ / S_\ell^- \gg_E \qquad (6\text{-}24f)$$

$$\left(\begin{smallmatrix}0\\k-q\end{smallmatrix}, \begin{smallmatrix}+\\q\end{smallmatrix}\right| \equiv \left(\begin{smallmatrix}0\\k-q\end{smallmatrix}, \begin{smallmatrix}+\\q\end{smallmatrix}\middle|\begin{smallmatrix}-\\-k\end{smallmatrix}\right)$$

$$= \sum_{\ell}\sum_{r}\sum_{s} e^{i(k-q)\cdot r} e^{iq\cdot s} e^{-iq\cdot\ell}\left(\begin{smallmatrix}z\\r\end{smallmatrix}\begin{smallmatrix}+\\s\end{smallmatrix}\middle|\begin{smallmatrix}-\\\ell\end{smallmatrix}\right) \qquad (6\text{-}24g)$$

$$\left(\begin{smallmatrix}z\\r\end{smallmatrix}\begin{smallmatrix}+\\s\end{smallmatrix}\middle|\begin{smallmatrix}-\\\ell\end{smallmatrix}\right) = \left[\begin{smallmatrix}z\\r\end{smallmatrix}\begin{smallmatrix}+\\s\end{smallmatrix}\middle|\begin{smallmatrix}-\\\ell\end{smallmatrix}\right] - \langle S_r^z\rangle\left[\begin{smallmatrix}+\\s\end{smallmatrix}\middle|\begin{smallmatrix}-\\\ell\end{smallmatrix}\right] \qquad (6\text{-}24h)$$

$$= \ll S_r^z S_s^+ / S_\ell^- \gg_E - \langle S_r^z\rangle \ll S_s^+ / S_\ell^- \gg_E$$

has been employed.

g_k^+, $g_{k-q,q}^{0\,+}$, $\gamma_{k-q,q-k}^{0\,0}$, and $\gamma_{-q,q}^{-\,+}$ are Fourier transforms of certain linear combinations of thermal averages.

Note that $G_0 = \left(\begin{smallmatrix}+\\0\end{smallmatrix}\right| \equiv \left(\begin{smallmatrix}+\\k\end{smallmatrix}\right|_{k=0}$. (6-25)

Equations (6-23) are easily solved for $\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right|$. The solution is

$$\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| = \frac{g_k^+ + \sum_q \frac{a_0(k,q)}{E-\Delta_0(q)}}{E-\Delta_0(k) - \sum_q a^2(k,q)/[E-\Delta_0(q)]} \qquad (6\text{-}26)$$

where

$$a_0(k,q) = \frac{1}{N} D(q,k-q)\, g_{k-q,q}^{0\,+} \qquad (6\text{-}27a)$$

$$a^2(k,q) = \frac{1}{N^2} D(q,k-q)\, R(k,q) \qquad (6\text{-}27b)$$

Equation (6-26) does not satisfy the complexity requirement for high temperatures, as

$$\Delta_0(q) \longrightarrow \omega_0 \qquad (T \text{ large}) \tag{6-28}$$

and $g_{BA}(\omega)$ reduces to a sum of two delta-functions.

The first two Fourier-transformed second-stage EOR-decoupled equations, derived from the spatial equations (6-8) are

$$\{E - \Delta_0(k)\}\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| = g_k^+ + (1/N)\sum_q D(q, k-q)\left(\begin{smallmatrix}0 & +\\k-q & q\end{smallmatrix}\right| \tag{6-29a}$$

$$\{E - \Delta_0(q)\}\left(\begin{smallmatrix}0 & +\\k-q & q\end{smallmatrix}\right| = g_{k-q\,q}^{0\,+} + (1/N) R(k,q)\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right|$$

$$+ \left[(1/N) P(k,q)\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| + (1/N)\sum_{k'} Q(k,q,k')\left(\begin{smallmatrix}0 & +\\k-k' & k'\end{smallmatrix}\right|\right] \tag{6-29b}$$

where

$$P(k,q) = (1/N)\sum_{k'}\{C(k+k'-q, k-q-k')\,\gamma_{-k'\,k'}^{-\,+} + C(k+k'-q, k')\,\gamma_{-k'\,k'}^{-\,+} - D(k'-q, k')\,\gamma_{-k'\,k'}^{0\,0}\}; \tag{6-30a}$$

$$Q(k,q,k') = \tfrac{1}{2} D(k', k-k') - 2\mu D(k', k'-q) - \mu D(k-k'-q, k-k'). \tag{6-30b}$$

To solve equations (6-29) formally for $\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right|$, we treat the terms in the square bracket of equation (6-29b) as sufficiently small, compared to $(1/N) R(k,q)\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right|$ so that an iteration procedure can be used; this is equivalent to the recognition that the EOR and T-T methods do not diverge widely from one another. Letting

$$\mathcal{R}(k,q) = R(k,q) + P(k,q)\,, \tag{6-31}$$

the second EOR equation, (6-29b), may be written

$$\{E-\Delta_0(q)\}\left(\begin{smallmatrix}0\\k-q\end{smallmatrix},\begin{smallmatrix}+\\q\end{smallmatrix}\right| = g^{0}_{k-q}\,g^{+}_{q} + \frac{1}{N}R(k,q)\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| + (1/N)\sum_{k'}Q(k,q,k')\left(\begin{smallmatrix}0\\k-k'\end{smallmatrix},\begin{smallmatrix}+\\k'\end{smallmatrix}\right| \quad (6\text{-}32)$$

or, with the use of the iteration procedure on $\left(\begin{smallmatrix}0\\k-q\end{smallmatrix}\begin{smallmatrix}+\\q\end{smallmatrix}\right|$,

$$\{E-\Delta_0(q)\}\left(\begin{smallmatrix}0\\k-q\end{smallmatrix}\begin{smallmatrix}+\\q\end{smallmatrix}\right| = S_E(k,q) + (1/N)\,\mathcal{S}_E(k,q)\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| \quad (6\text{-}33)$$

where

$$S_E(k,q) = g^{0}_{k-q}\,g^{+}_{q} + (1/N)\sum_{k'}\frac{Q(k,q,k')}{E-\Delta_0(k')}\,g^{0}_{k-k'}\,g^{+}_{k'} + (1/N^2)\sum_{k'}\sum_{k''}\frac{Q(k,q,k')\,Q(k,k',k'')}{(E-\Delta_0(k'))(E-\Delta_0(k''))}\,g^{0}_{k-k''}\,g^{+}_{k''} + \cdots \quad (6\text{-}34)$$

We note that $S_E(k,q)$ satisfies the "integral equation"

$$S_E(k,q) = g^{0}_{k-q}\,g^{+}_{q} + (1/N)\sum_{k'}\frac{Q(k,q,k')}{E-\Delta_0(k')}\,S_E(k,k'). \quad (6\text{-}35)$$

Similarly, $\mathcal{S}_E(k,q)$ satisfies the "integral equation"

$$\mathcal{S}_E(k,q) = R(k,q) + (1/N)\sum_{k'}\frac{Q(k,q,k')}{E-\Delta_0(k')}\,\mathcal{S}_E(k,k'). \quad (6\text{-}36)$$

Equations (6-29), solved simultaneously, yield the formal expression

$$\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right| = \frac{g^{+}_{k} + \frac{1}{N}\sum_{q}\frac{D(q,k-q)\,S_E(k,q)}{E-\Delta_0(q)}}{E-\Delta_0(k) - \frac{1}{N^2}\sum_{q}\frac{D(q,k-q)\,\mathcal{S}_E(k,q)}{E-\Delta_0(q)}}. \quad (6\text{-}37)$$

One would like to solve equations (6-35) and (6-36) exactly for $\mathcal{S}_E(k,q)$ and $\mathcal{S}_E(k,q)$ respectively. Unfortunately, this cannot readily be done, as the coefficients in these equations do not possess convenient symmetry properties. Let us, however, consider the simple case when

$$Q(k,q,k') = Q(k,q,q)\,\delta_{k'q} \quad . \tag{6-38}$$

Equations (6-35) and (6-36) then have the solutions

$$\mathcal{S}_E(k,q) = \frac{g^{\circ}_{k-q,\,q}\,{}^{+}}{1 - \frac{1}{N}\frac{Q(k,q,q)}{E-\Delta_0(q)}} \tag{6-39}$$

$$\mathcal{S}_E(k,q) = \frac{R(k,q)}{1 - \frac{1}{N}\frac{Q(k,q,q)}{E-\Delta_0(q)}} \quad , \tag{6-40}$$

Substituting (6-39) and (6-40) into equation (6-37), we get the following expression for $\langle {}^{+}_{k}|$:

$$\left\langle {}^{+}_{k}\right| = \frac{g^{+}_{k} + \frac{1}{N}\sum_{q}\frac{D(q,k-q)\,g^{\circ}_{k-q,\,q}\,{}^{+}}{E-\Delta_0(q)-\frac{1}{N}Q(k,q,q)}}{E-\Delta_0(k)-\frac{1}{N^2}\sum_{q}\frac{D(q,k-q)\,R(k,q)}{E-\Delta_0(q)-\frac{1}{N}Q(k,q,q)}} \quad , \tag{6-41}$$

Equation (6-41) satisfies the complexity requirement even in the high-temperature limit for which (6-28) holds. We note that this requirement is also satisfied when equation (6-41) is specialized to the Ising model case, when (see equation (6-47))

$$\Delta_0(q) = \Delta_0 \quad \text{independent of q} \qquad (6\text{-}42)$$

The latter statement cannot be made about equation (6-26), the equivalent T-T solution. It will be demonstrated, in the next section, that also 3rd-stage T-T decoupling is not "complex" enough for the Ising model case.

3. Complexity Requirement

We have seen above that at second-stage decoupling the EOR method satisfies the complexity requirement that the line shape consist of many delta-functions. In order to have this requirement satisfied with Tomita-Tanaka decoupling, these authors had to go to a third-stage decoupling. In this section, we shall discuss this point.

Using third-stage decoupling, Tomita and Tanaka arrived at a closed set of equations which proved to be quite tractable, having as a solution

$$(\overset{+}{k}| = \mathcal{N}^+ / \mathcal{D}^+ \qquad (6\text{-}43)$$

with

$$\mathcal{D}^+ = E - \Delta_0(k) - \sum_q \frac{a^2(k,q) - \sum_{q'} \frac{c^3(k,q,q')}{E - \Delta_0(q')}}{E - \Delta_0(q) - \sum_{q'} \frac{b^2(k,q,q')}{E - \Delta_0(q')}} \; ; \qquad (6\text{-}44a)$$

$$n^{+} = g_{k}^{+} + \sum_{q} \frac{a_0(k,q) + \sum_{q'} \frac{c_0^2(k,q,q')}{E - \Delta_0(q')}}{E - \Delta_0(q) - \sum_{q'} \frac{b^2(k,q,q')}{E - \Delta_0(q')}} \qquad (6\text{-}44b)$$

where $c_0^2(k,q,q')$ and $c^3(k,q,q')$ involve Fourier transforms of A_{ij}, C_{ij}, and of certain linear combinations of thermal averages, and

$$b^2(k,q,q') = D(q',q-q')\left\{D(q,q'-q)\,\gamma^{\circ}_{q-q',\,q'-q} + C(q',q)\,\gamma^{-+}_{q',\,-q'}\right\}$$
$$+ C(q',k-q-q')\left\{D(q',k-q)\,\gamma^{+-}_{-q',\,q'} - D(q+q'-k,k-q)\,\gamma^{+-}_{k-q-q',\,q+q'-k}\right\}. \qquad (6\text{-}45)$$

Equation (6-43) can, by use of the method of partial fractions, be cast into a form which leads to a sum of delta-functions for the line shape. These must be smeared in some way so that a continuous line shape function results. One can perform this smearing only if the delta-functions are sufficiently large in number, and their arguments sufficiently dense along the ω-axis. It is this condition that has been referred to as the complexity requirement.#

At first sight, Tomita and Tanaka's expression (6-43) for $\left(\begin{smallmatrix}+\\k\end{smallmatrix}\right|$ seems to satisfy the complexity requirement. It especially seems to do so for the general paramagnetic case. However, it demonstrably does not for the case of the general Ising model, at any temperature and for any spin. This will now be shown.

Grant and Strandberg (1964) satisfied this complexity requirement by treating the distribution of spins well-removed from the one of interest as continuous.

Recall that for the general Ising model (2-27)

$$A_{ij} = 0 \tag{6-46a}$$

i.e.,

$$A(q) = 0 \qquad \text{all } q. \tag{6-46b}$$

As a consequence, the quantities $\Delta_0(q)$ and $b^2(k,q,q')$ involved in equation (6-43) become

$$\Delta_0(q) = \omega_0 + \mu C(0) \equiv \Delta_0 \qquad \text{independent of q} \tag{6-47}$$

and

$$b^2(k,q,q') = C^2(q-q')\,\gamma^0_{q-q';\,q'-q} \equiv b^2(k,q-q'). \tag{6-48}$$

Then $\mathcal{D}^+$ and $\mathcal{N}^+$ (equations (6-44a) and (6-44b)) become

$$\mathcal{D}^+ = E - \Delta_0 - \sum_q \frac{a^2(k,q) - (E-\Delta_0)^{-1}\sum_{q'} c^3(k,q,q')}{E-\Delta_0-(E-\Delta_0)^{-1}\sum_{q'} b^2(k,q-q')}; \tag{6-49a}$$

$$\mathcal{N}^+ = g_k^+ + \sum_q \frac{a_0(k,q) + (E-\Delta_0)^{-1}\sum_{q'} c_0^2(k,q,q')}{E-\Delta_0-(E-\Delta_0)^{-1}\sum_{q'} b^2(k,q-q')}. \tag{6-49b}$$

Now

$$\sum_{q'} b^2(k,q-q') = \sum_{q'} b^2(k,q') \equiv b^2(k) \tag{6-50}$$

by translational invariance. So, if we define $a_0(k)$, $c_0^2(k)$, $c^3(k)$ and $a^2(k)$ as follows

$$
\begin{aligned}
a_0(k) &\equiv \sum_{q} a_0(k,q) \\
c_0^2(k) &\equiv \sum_{q} \sum_{q'} c_0^2(k,q,q') \\
a^2(k) &\equiv \sum_{q} a^2(k,q) \\
c^3(k) &\equiv \sum_{q} \sum_{q'} c^3(k,q,q')
\end{aligned}
\tag{6-51}
$$

we may write

$$
\left(\begin{matrix} + \\ k \end{matrix} \middle| = \frac{g_k^+ + \dfrac{a_0(k) + (E-\Delta_0)^{-1} c_0^2(k)}{E-\Delta_0 - (E-\Delta_0)^{-1} b^2(k)}}{E-\Delta_0 - \dfrac{a^2(k) - (E-\Delta_0)^{-1} c^3(k)}{E-\Delta_0 - (E-\Delta_0)^{-1} b^2(k)}} \right. ,
\tag{6-52}
$$

This yields, via (6-25) and (5-40), a line shape function which is expressed as a sum of three delta-functions. It is, of course, wrong to extrapolate from these to a continuous line shape function.

Now, the general Ising model admits interaction of any spin with all its neighbours, no matter how far away. The most elementary considerations indicate that unless one is dealing with the one-dimensional Ising model with S = ½, nearest-neighbour interactions, many more than three delta functions

are required to describe the line shape. One must conclude that Tomita and Tanaka's third-stage decoupling cannot be used on the Ising model with any success.

4. Application to Case of Completely Non-equidistant Single-Spin Energy Levels.

This chapter so far has considered the case in which the single-spin energy levels are equally spaced. The most fruitful approach to the case of completely non-equidistant energy levels would appear to be through the use of the operators $A_{i\lambda}^{\pm}$ introduced in Chapter II.

This, however, proves sufficiently complicated, even with T-T decoupling, that it is unlikely to yield a line shape, and one has to be content with calculations of moments as in Chapter IV. To see this, let us discuss first-stage decoupling and indicate what would happen in second-stage decoupling.

The statement that the unperturbed energy levels are completely non-equidistant implies that whenever

$$\overline{T}_{\lambda'+1} - \overline{T}_{\lambda'} = \overline{T}_{\lambda+1} - \overline{T}_{\lambda} \quad ,$$

one has

$$\lambda' = \lambda \tag{6-53}$$

This is a restriction on the elements of the set G defined in Chapter II. The Hamiltonian $\overline{\mathcal{H}}$ can then be written as (see equation (2-23))

$$\overline{\mathcal{H}} = \sum_i \mathcal{H}_i^{(0)} + \frac{1}{2} \sum_{i \neq j} \sum \left\{ \left(A_{ij} \sum_{\lambda'} A_{i\lambda'+1}^{-} A_{j\lambda'}^{+} \right) + C_{ij} S_i^z S_j^z \right\} \tag{6-54}$$

where $\mathcal{H}_i^{(0)}$ is defined by equation (2-16).

We will take the unperturbed frequency, ω_o ,of the primary line under consideration to be given by

$$\omega_o = T_{\lambda+1} - T_\lambda \quad . \tag{6-55}$$

We then look for

$$G_{o\,|\varepsilon} = \sum_i \sum_\ell \langle\langle S_{i\lambda}^+ \,|\, S_{\ell\lambda+1}^- \rangle\rangle_\varepsilon \tag{6-56}$$

in order to find the line shape function

$$g(\omega) = \frac{\lim_{\varepsilon\to 0^+} \mathrm{Im}\, G_{o\,|\omega-i\varepsilon}}{\lim_{\varepsilon\to 0^+} \int d\omega\, \mathrm{Im}\, G_{o\,|\omega-i\varepsilon}} \quad . \tag{6-57}$$

The first Green's function equation is

$$\begin{aligned} e\left[S_{m\lambda}^+ \right| = {} & \frac{1}{2\pi} \left\langle \left[S_{m\lambda}^+ , S_{\ell\lambda+1}^- \right] \right\rangle \\ & + \frac{1}{2} \sum_j A_{mj} \left[\left[S_{m\lambda}^+ , S_{m\lambda+1}^- \right] S_{j\lambda}^+ \right| \\ & + \frac{1}{2} \sum_j A_{mj} \left[S_{j\lambda}^- S_{m\lambda}^+ S_{m\lambda-1}^+ - S_{j\lambda+2}^- S_{m\lambda+1}^- S_{m\lambda}^+ \right| \\ & - \frac{1}{2} \sum_{\lambda'} \sum_j C_{mj} \left[S_{m\lambda}^+ \left[S_{j\lambda'}^+ , S_{j\lambda'+1}^- \right] \right| \end{aligned} \tag{6-58}$$

where we have used the relation

$$\begin{aligned} S_i^z &= \frac{1}{2} \sum_\lambda \left[S_{i\lambda}^+ , S_{i\lambda+1}^- \right] \\ &\equiv \sum_\lambda S_{i\lambda}^z \end{aligned} \tag{6-59}$$

which follows from

$$[S_i^+, S_i^-] = 2 S_i^z$$

combined with (2-32) and (2-22).

T-T decoupling in the first stage consists, here, in performing the decomposition (6-3c) and neglecting higher-order cumulant Green's functions. This is equivalent to making replacements like the following:

$$[A_{m\lambda}^+ A_{m\lambda+1}^- A_{j\lambda}^+ | \longrightarrow \langle A_{m\lambda}^+ A_{m\lambda+1}^- \rangle (A_{j\lambda}^+| + \langle A_{m\lambda+1}^- A_{j\lambda}^+ \rangle (A_{m\lambda}^+| \; ;$$

$$[A_{m\lambda+1}^- A_{m\lambda}^+ A_{j\lambda}^+ | \longrightarrow \langle A_{m\lambda+1}^- A_{m\lambda}^+ \rangle (A_{j\lambda}^+| + \langle A_{m\lambda+1}^- A_{j\lambda}^+ \rangle (A_{m\lambda}^+| \; .$$

With this decoupling, equation (6-58) becomes

$$\begin{aligned} e\,(A_{m\lambda}^+| = {} & \frac{1}{2\pi} \langle [A_{m\lambda}^+, A_{\ell\lambda+1}^-] \rangle + \sum_j A_{mj} \langle A_{m\lambda}^z \rangle (A_{j\lambda}^+| \\ & + \frac{1}{2} \sum_j A_{mj} \langle A_{j\lambda}^- A_{m\lambda-1}^+ \rangle (A_{m\lambda}^+| \\ & - \frac{1}{2} \sum_j A_{mj} \langle A_{j\lambda+2}^- A_{m\lambda+1}^+ \rangle (A_{m\lambda}^+| \\ & - \sum_j C_{mj} \langle S_j^z \rangle (A_{m\lambda}^+| \; . \end{aligned}$$

(6-60)

Taking Fourier transforms as in Section 2 and using (6-56) and (6-57), one gets a single delta-function for the line shape:

$$g(\omega) = \delta\Big\{\omega - \omega_0 - \mu_\lambda^2 A(k) + \mu C(0) - \frac{1}{2N^2}\sum_{k'}\Big(\big\langle \bar{k}'_{,\lambda}\ \ \bar{k}'_{,\lambda-1}\big\rangle - \big\langle \bar{k}'_{,\lambda+2}\ \ \bar{k}'_{,\lambda+1}\big\rangle\Big)A(k')\Big\} \tag{6-61}$$

where $\mu_\lambda^2 \equiv \langle S_{i\lambda}^2 \rangle$ independent of i ;

$\mu = \langle S_i^z \rangle$ independent of i ;

$$\big\langle \bar{k}'_{,\lambda}\ \ \bar{k}'_{,\lambda-1}\big\rangle \equiv \sum_m \sum_j e^{ik'\cdot m} e^{-ik'\cdot j} \big\langle S^-_{m\lambda}\, S^+_{j\lambda-1}\big\rangle .$$

In deriving equation (6-61), one had simply to solve one equation for

$$\big(k^+_{,\lambda}\big| \equiv \sum_j e^{ik\cdot j}\big(S^+_{j\lambda}\big| \quad .$$

To see the difficulties that arise when second-stage decoupling is attempted, consider the simplest case, that of effective spin S = 1 (with λ = -1, say, in (6-55)). One must keep all Green's functions of the form

$$\big(S^+_{i,-1}, S^+_{j,0}, S^-_{m,1}\big| \ , \ \big(S^+_{i,-1}, S^-_{j,0}, S^+_{m,-1}\big| \ , \ \ldots$$

where there are two S^+'s and one S^- in each Green's function. There are nine of these, seven of which are independent. A separate Green's function equation must be written for each of these seven, a decomposition made, on the right hand side of each equation, of higher-order Green's functions into lower-order ones, according to equations (6-3), and Fourier transforms taken. One then has, optimistically, seven coupled simultaneous linear equations to

solve. The latter number increases quickly when higher spins are used. This process is quite unwieldy, and so the analysis has not been pursued any further.

5. Summary of Chapter VI.

We have, in this chapter, applied a moment theorem to compare the faithfulness of two decoupling techniques. The results of the comparison are summarized in the table on page 61 . The EOR decoupling proves more faithful than T-T decoupling, but unfortunately, less tractable. It satisfies the complexity requirement at second-stage decoupling, whereas T-T decoupling satisfies this requirement only with a third-stage decoupling. For the Ising model, this complexity is not satisfied even with 3rd-stage T-T decoupling.

The argument in favour of Tomita and Tanaka's approach to the general paramagnetic resonance line shape problem is that it does, at least in the case of equally-spaced unperturbed energy levels, provide an analytic line shape function. This may be more important than its providing correct moments.

APPENDIX I

To show that in

$$T^{ji} \equiv \left\langle \left[S_j^-, e^{-i\bar{\mathcal{H}}^{(1)}t} \sum_{\lambda \in G_1} A_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t} \right] \right\rangle, \tag{A-1}$$

$S_j^- \equiv \sum_{\lambda'} A_{j\lambda'+1}^-$ may be replaced by $\sum_{\lambda' \in G_1} A_{j\lambda'+1}^-$.

Now,

$$\left(T_\lambda e^{-\beta\bar{\mathcal{H}}}\right) T^{ji} = \sum_{\lambda'} \sum_{\lambda \in G_1} \langle \alpha | e^{-\beta\bar{\mathcal{H}}} \left[A_{j\lambda'+1}^-, e^{-i\bar{\mathcal{H}}^{(1)}t} A_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t} \right] | \alpha \rangle \tag{A-2}$$

where we have expanded the trace in terms of eigenstates $|\alpha\rangle$ of $\mathcal{H}^{(0)}$ with eigenvalues E_α .

Let

$$M_{\lambda'\lambda}^{\alpha ji} = \langle \alpha | e^{-\beta\bar{\mathcal{H}}} A_{j\lambda'+1}^- e^{-i\bar{\mathcal{H}}^{(1)}t} A_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t} | \alpha \rangle \tag{A-3}$$

Then

$$E_\alpha M_{\lambda'\lambda}^{\alpha ji} = \langle \alpha | e^{-\beta\bar{\mathcal{H}}} A_{j\lambda'+1}^- e^{-i\bar{\mathcal{H}}^{(1)}t} A_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t} \mathcal{H}^{(0)} | \alpha \rangle . \tag{A-4}$$

Using (2-8), (2-21), and the hermiticity of $\mathcal{H}^{(0)}$, we have

$$\begin{aligned} E_\alpha M_{\lambda'\lambda}^{\alpha ji} &= \langle \alpha | \mathcal{H}^{(0)} e^{-\beta\bar{\mathcal{H}}} A_{j\lambda'+1}^- e^{-i\bar{\mathcal{H}}^{(1)}t} A_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t} | \alpha \rangle \\ &\quad + \langle \alpha | \left[e^{-\beta\bar{\mathcal{H}}} A_{j\lambda'+1}^- e^{-i\bar{\mathcal{H}}^{(1)}t} A_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t}, \mathcal{H}^{(0)} \right] | \alpha \rangle \\ &= E_\alpha M_{\lambda'\lambda}^{\alpha ji} + \langle \alpha | e^{-\beta\bar{\mathcal{H}}} A_{j\lambda'+1}^- e^{-i\bar{\mathcal{H}}^{(1)}t} \left[A_{i\lambda}^+, \mathcal{H}^{(0)} \right] e^{+i\bar{\mathcal{H}}^{(1)}t} | \alpha \rangle \\ &\quad + \langle \alpha | e^{-\beta\bar{\mathcal{H}}} \left[A_{j\lambda'+1}^-, \mathcal{H}^{(0)} \right] e^{-i\bar{\mathcal{H}}^{(1)}t} A_{i\lambda}^+ e^{i\bar{\mathcal{H}}^{(1)}t} | \alpha \rangle \\ &= E_\alpha M_{\lambda'\lambda}^{\alpha ji} + \left(T_{\lambda+1} - T_\lambda\right) M_{\lambda'\lambda}^{\alpha ji} - \left(T_{\lambda'+1} - T_{\lambda'}\right) M_{\lambda'\lambda}^{\alpha ji} . \end{aligned} \tag{A-5}$$

Therefore

$$\left[(T_{\lambda'+1} - T_{\lambda'}) - (T_{\lambda+1} - T_{\lambda}) \right] M_{\lambda'\lambda}^{\alpha j i} = 0 \quad . \tag{A-6}$$

But, for $\lambda \in G_1$, $T_{\lambda+1} - T_{\lambda} = \omega_0$ (see equation (2-31)).

So

$$\underset{(\lambda \in G_1)}{M_{\lambda'\lambda}^{\alpha j i}} = \delta_{T_{\lambda'+1} - T_{\lambda'},\, \omega_0} \, M_{\lambda'\lambda}^{\alpha j i} \tag{A-7}$$

i.e., $M_{\lambda'\lambda}^{\alpha j i}$ $(\lambda \in G_1)$ is zero unless $\lambda' \in G_1$.

Similarly,

$$\underset{(\lambda \in G_1)}{N_{\lambda'\lambda}^{\alpha j i}} = \delta_{T_{\lambda'+1} - T_{\lambda'},\, \omega_0} \, N_{\lambda'\lambda}^{\alpha j i} \tag{A-8}$$

where

$$N_{\lambda'\lambda}^{\alpha j i} \equiv \langle \alpha | e^{-\beta \bar{\mathcal{H}}} e^{-i \bar{\mathcal{H}}^{(1)} t} \Delta_{i\lambda}^{+} e^{i \bar{\mathcal{H}}^{(1)} t} \Delta_{j\lambda'+1}^{-} | \alpha \rangle \quad . \tag{A-9}$$

From (A-8), (A-7), (A-9), (A-3), and (A-2),

$$T^{ji} = \left\langle \left[\sum_{\lambda' \in G_1} \Delta_{j\lambda'+1}^{-}, e^{-i \bar{\mathcal{H}}^{(1)} t} \sum_{\lambda \in G_1} \Delta_{i\lambda}^{+} e^{i \bar{\mathcal{H}}^{(1)} t} \right] \right\rangle \tag{A-10}$$

APPENDIX II

Calculation of Thermal Averages for the One-Dimensional Ising Model using a Difference Equation Technique.

As an illustration of the technique, the derivation of the thermal average $Z\langle 1\rangle$ will be given.

$$Z\langle 1\rangle = Z\langle S_i^z\rangle \qquad \text{independent of } i$$

$$= Tr\left(e^{-\beta\mathcal{H}} S_N^z\right) \qquad \text{where we have taken } i = N$$

$$= \sum_{\eta_1\eta_2\cdots\eta_N} (\eta_1)(\eta_2)\cdots(\eta_N)(\eta_1\eta_2)(\eta_2\eta_3)\cdots(\eta_{N-1}\eta_N)(\eta_N\eta_1) \underbrace{\langle\eta_N|S_N^z|\eta_N\rangle} \qquad \text{(A-11)}$$

where $|\eta_i\rangle$, η_i are eigenstates and eigenvalues of S_i^z, i.e.

$$S_i^z|\eta_i\rangle = \eta_i|\eta_i\rangle \qquad \text{(A-12)}$$

and η_i can assume the values $\pm 1/2$; $\beta = 1/kT$; and the following notation is used:

$$(\eta_i) \equiv \langle\eta_i|b^{S_i^z}|\eta_i\rangle \; ; \; b = e^{\beta h} \; ; \qquad \text{(A-13)}$$

$$(\eta_i\eta_{i+1}) \equiv \langle\eta_i|\langle\eta_{i+1}|c^{S_i^z S_{i+1}^z}|\eta_{i+1}\rangle|\eta_i\rangle \; ; \; c = e^{\beta\epsilon} \; . \qquad \text{(A-14)}$$

We will also use

$$\langle\eta_i^+\rangle \equiv \langle\eta_i|c^{\pm S_i^z}|\eta_i\rangle \qquad \text{(A-15a)}$$

$$\langle\eta_i^-\rangle \equiv \langle\eta_i|c^{-\pm S_i^z}|\eta_i\rangle \qquad \text{(A-15b)}$$

$$\alpha = c^{1/4} b^{1/2} \tag{A16a}$$

$$\gamma = c^{-1/4} b^{-1/2} \tag{A-16b}$$

$$\beta = c^{-1/4} b^{1/2} \tag{A-16c}$$

$$\delta = c^{1/4} b^{-1/2} \tag{A-16d}$$

Performing the summation over n_N ,

$$Z\langle 17\rangle = \sum_{n_1,\ldots,n_{N-1}} (n_1)\ldots(n_{N-1})(n_1 n_2)\ldots(n_{N-2} n_{N-1}) \times \left[\tfrac{1}{2} b^{1/2} \langle n_1^+\rangle\langle n_{N-1}^+\rangle - \tfrac{1}{2} b^{-\frac{1}{2}} \langle n_1^-\rangle\langle n_{N-1}^-\rangle\right], \tag{A-17}$$

Looking at the first term on the R.H.S. of (A-17), we write it in the following way:

$$\left(Z\langle 17\rangle\right)_1 = \frac{b^{1/2}}{2} \sum_{n_1,\ldots,n_{N-1}} \langle n_1^+\rangle (n_1)(n_1 n_2)(n_2)(n_2 n_3)\ldots \ldots (n_{N-2})(n_{N-2} n_{N-1})(n_{N-1})\langle n_{N-1}^+\rangle. \tag{A-18}$$

Noting that

$$\sum_{n_i} \langle n_i^+\rangle (n_i)(n_i n_{i+1}) = \alpha \langle n_{i+1}^+\rangle + \gamma \langle n_{i+1}^-\rangle \tag{A-19a}$$

and

$$\sum_{n_i} \langle n_i^-\rangle (n_i)(n_i n_{i+1}) = \beta \langle n_{i+1}^+\rangle + \delta \langle n_{i+1}^-\rangle \tag{A-19b}$$

it follows that equation (A-18), after it is summed over $n_1, n_2, \ldots, n_p$ $(p \leq N-2)$,

may be written in the form

$$\left(\sum \langle \eta \rangle\right)_1 = \frac{b^{1/2}}{2} \sum_{n_{p+1} \cdots n_{N-1}} \left(a_{p+1} \langle \eta_{p+1}^{+} \rangle + b_{p+1} \langle \eta_{p+1}^{-} \rangle\right)$$

$$\times (\eta_{p+1})(\eta_{p+1}\eta_{p+2}) \cdots \langle \eta_{N-1}^{+} \rangle \qquad \text{(A-20)}$$

where a_p and b_p satisfy the recursion relations

$$a_{p+1} = \alpha a_p + \beta b_p \qquad \text{(A-21a)}$$

$$b_{p+1} = \gamma a_p + \delta b_p \qquad \text{(A-21b)}$$

with the initial conditions $b_1 = 0$, $a_1 = 1$.

Equations (A-21) can easily be cast into the form of a pair of second-order difference equations:

$$b_{p+1} - (\alpha + \delta) b_p - (\beta\gamma - \alpha\delta) b_{p-1} = 0 \quad \text{with} \quad b_1 = 0, \; b_2 = \gamma \; ; \qquad \text{(A-22a)}$$

$$a_{p+1} - (\alpha + \delta) a_p - (\beta\gamma - \alpha\delta) a_{p-1} = 0 \quad \text{with} \quad a_1 = 1, \; a_2 = \alpha \; . \qquad \text{(A-22b)}$$

Equations (A-22) possess the solutions

$$a_p = F_a (\lambda_+)^p + G_a (\lambda_-)^p \qquad \text{(A-23a)}$$

$$b_p = F_b (\lambda_+)^p + G_b (\lambda_-)^p \qquad \text{(A-24b)}$$

where F_a, F_b, G_a, G_b are independent of p and are determined from the initial conditions, and $\lambda_\pm$ are given by equation (3-13).

In the calculation of the second term of equation (A-17), one has occasion to look at the equations

$$C_{p+1} = \alpha C_p + \beta d_p \qquad \text{(A-25a)}$$

$$d_{p+1} = \gamma C_p + \delta d_p \qquad \text{(A-25b)}$$

with initial conditions $C_1 = 0$, $d_1 = 1$.
They possess solutions

$$C_p = F_c (\lambda_+)^p + G_c (\lambda_-)^p \qquad \text{(A-26a)}$$

$$d_p = F_d (\lambda_+)^p + G_d (\lambda_-)^p \qquad \text{(A-26b)}$$

where F_c, G_c, F_d, G_d are again determined from the initial conditions.

Whatever thermal averages are done, one can always arrange the terms in the appropriate summations in such a way that either (A-21) or (A-25) need be used for each term. A list of the values of the F's and G's follows, where the notation

$$\sqrt{\quad} \equiv \sqrt{(\alpha - \delta)^2 + 4\beta\gamma} \qquad \text{(A-27)}$$

is used.

F_a	$(\alpha-\delta+\sqrt{\ })/(\alpha+\delta+\sqrt{\ })\sqrt{\ }$	G_a	$(\delta-\alpha+\sqrt{\ })/(\alpha+\delta-\sqrt{\ })\sqrt{\ }$
F_b	$2\gamma/(\alpha+\delta+\sqrt{\ })\sqrt{\ }$	G_b	$-2\gamma/(\alpha+\delta-\sqrt{\ })\sqrt{\ }$
F_c	$2\beta/(\alpha+\delta+\sqrt{\ })\sqrt{\ }$	G_c	$-2\beta/(\alpha+\delta-\sqrt{\ })\sqrt{\ }$
F_d	$(\delta-\alpha+\sqrt{\ })/(\alpha+\delta+\sqrt{\ })\sqrt{\ }$	G_d	$(\alpha-\delta+\sqrt{\ })/(\alpha+\delta-\sqrt{\ })\sqrt{\ }$

From the above table, the following relations can easily be constructed and are found to be useful:

$$d_p = a_p + \frac{\delta-\alpha}{\gamma} b_p \ ; \qquad \text{(A-28a)}$$

$$\beta b_p = \gamma c_p \ . \qquad \text{(A-28b)}$$

Continuing from equation (A-20), performing the final summations, and using equations (A-21), we have

$$(z\langle 1\rangle)_1 = \frac{b^{1/2}}{2} \sum_{n_{N-1}} (a_{N-1}\langle n_{N-1}^+\rangle + b_{N-1}\langle n_{N-1}^-\rangle)(n_{N-1})\langle n_{N-1}^+\rangle$$

$$= \frac{1}{2} a_{N+1} \ . \qquad \text{(A-29)}$$

Similarly, the second term of (A-17), which we call $(z\langle 1\rangle)_2$, is given by

$$(z\langle 1\rangle)_2 = -\frac{1}{2} d_{N+1} \qquad \text{(A-30)}$$

and so

$$Z\langle 17\rangle = (Z\langle 17\rangle)_1 + (Z\langle 17\rangle)_2$$

$$= \frac{1}{2}(a_{N+1} - d_{N+1})$$

$$= \frac{1}{2}\frac{\alpha-\delta}{\gamma} b_{N+1}, \text{ from (A-28a).} \qquad \text{(A-31)}$$

One similarly finds that the partition function Z is given by

$$Z = a_{N+1} + d_{N+1}$$

$$= (F_a + F_d)(\lambda_+)^{N+1} + (G_a + G_d)(\lambda_-)^{N+1}$$

$$= (\lambda_+)^N + (\lambda_-)^N \qquad \text{(A-32)}$$

as given by Huang (1963).

All other thermal averages can be found in the same way, when this is tractable. For example, the thermal average $\langle S_i^z S_{i+10}^z \rangle$ becomes cumbersome to find by this method, as eleven summations must be done explicitly before the difference equation solution can be applied.

APPENDIX III

Proof of (4-15) directly from (5-2a) and (5-3)

Let

$$F_E(t) = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} G_n(E) \quad ; \tag{A-33}$$

$$T(t) = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \overline{T_n} \quad . \tag{A-34}$$

Then

$$F_E(0) = G_0(E) \, . \tag{A-35}$$

Multiplying both sides of equation (5-2a) by $(it)^n/n!$ and summing over n from 0 to ∞ , one derives the equation

$$e F_E(t) = T(t) - i \frac{\partial}{\partial t} F_E(t) \tag{A-36}$$

which has as solution

$$F_E(t) = -i \int_{t_0}^{t} d\xi \, T(\xi) e^{ie(t-\xi)} \, . \tag{A-37}$$

A boundary condition is needed to fix t_0, the constant of integration. We make use of the fact that when $\overline{\mathcal{H}^{(1)}} = 0$, the hierarchy of equations (5-2a) reduces to the single equation

$$e G_0 = \overline{T_0} \tag{A-38}$$

and moreover,

$$T(\xi) = \overline{T_0} \, . \tag{A-39}$$

Substituting (A-39) into (A-37) and using (A-35),

$$e\, G_0(E) = T_0\,(1 - e^{-ie t_0}) \tag{A-40}$$

when $\bar{\mathcal{H}}^{(1)} = 0$. To make (A-40) correspond to (A-38), one needs

$$t_0 = +\infty \qquad (\mathrm{Im}\, E < 0) \tag{A-41}$$

The assumption is then made that (A-41) holds also when $\bar{\mathcal{H}}^{(1)} \neq 0$.

Now

$$\begin{aligned}
g_{BA}(\omega) \propto & \lim_{\varepsilon \to 0^+} \mathrm{Im}\, G_0(\omega - i\varepsilon) \\
= & \lim_{\varepsilon \to 0^+} \mathrm{Im}\, F_{\omega - i\varepsilon}(0) \\
= & \lim_{\varepsilon \to 0^+} \frac{1}{2i} \left\{ -i \int_{\infty}^{0} d\xi\, T(\xi)\, e^{-i(e - i\varepsilon)\xi} \right. \\
& \qquad \left. + i \int_{\infty}^{0} d\xi\, T^*(\xi)\, e^{i(e + i\varepsilon)\xi} \right\} \\
= & \lim_{\varepsilon \to 0^+} \frac{1}{2} \int_{-\infty}^{\infty} d\xi\, T(\xi)\, e^{-ie\xi - \varepsilon|\xi|} \\
= & \lim_{\varepsilon \to 0^+} \frac{1}{2} \int_{-\infty}^{\infty} d\xi \sum_{n=0}^{\infty} \frac{(i\xi)^n}{n!} T_n\, e^{-ie\xi - \varepsilon|\xi|}
\end{aligned} \tag{A-42}$$

where we have used the relation

$$\overline{T}^{*}(\xi) = \overline{T}(-\xi) \tag{A-43}$$

which follows from (A-34) and the reality of the $\overline{T}_n$. Equation (A-42) is equivalent to the stage reached in Chapter IV, equation (4-7), where a similar problem was considered. The proof is completed in essentially the same way, i.e., via the definition of a suitable characteristic function.

APPENDIX IV

Reality of A_α^ρ of equation (5-47)

It is assumed that T_α and C_α^β are real, as they are invariably simple known combinations of thermal averages.

From equation (5-51), $\sum_\rho (\varepsilon_\rho)^\ell A_\alpha^\rho$ are real for all α .

Let $A_\alpha^\rho(\mathcal{R})$ = Real part of A_α^ρ

$A_\alpha^\rho(\mathcal{I})$ = Imaginary part of A_α^ρ

Then

$$\sum_\rho (\varepsilon_\rho)^\ell A_\alpha^\rho(\mathcal{R}) + i \sum_\rho (\varepsilon_\rho)^\ell A_\alpha^\rho(\mathcal{I}) = \text{real} \quad , \tag{A-44}$$

i.e.

$$\sum_{\rho=1}^{n} (\varepsilon_\rho)^\ell A_\alpha^\rho(\mathcal{I}) = 0 \quad \text{all } \alpha, \ell . \tag{A-45}$$

Writing equation (A-45) in matrix form for ℓ having the values 0,1,2,...,n-1, i.e.

$$\begin{pmatrix} 1 & 1 & 1 & \cdots & 1 \\ \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \cdots & \varepsilon_n \\ (\varepsilon_1)^2 & (\varepsilon_2)^2 & \cdots & \cdots & (\varepsilon_n)^2 \\ \vdots & & & & \vdots \\ (\varepsilon_1)^{n-1} & & \cdots & & (\varepsilon_n)^{n-1} \end{pmatrix} \begin{pmatrix} A_\alpha^1(\mathcal{I}) \\ A_\alpha^2(\mathcal{I}) \\ \vdots \\ \vdots \\ A_\alpha^n(\mathcal{I}) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \end{pmatrix}$$

(A-46)

it is seen that the " $\mathcal{E}_\rho$ matrix", being a Vandermonde matrix and having all the $\mathcal{E}_\rho$ distinct, is non-singular, leading to the conclusion that

$$\begin{pmatrix} A'_\alpha(g) \\ \vdots \\ A^n_\alpha(g) \end{pmatrix} = \begin{pmatrix} 0 \\ \vdots \\ 0 \end{pmatrix} \qquad \text{(A-47)}$$

all α . This completes the proof.

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